Guanidines and Their Anions: Versatile Ligands for Metallo-organic Chemistry

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Declaration

I declare that this thesis has been entirely composed by myself and that the work described herein is my own except where clearly mentioned either in acknowledgement, reference or text. It has not been submitted in whole or in part, for any other degree. Certain of the results have already been published.
Acknowledgements

There are a number of people whom I would like to thank, without whose help this thesis would have been impossible.

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Abstract

There are a large number of highly stable systems which are isostructural and isoelectronic to carboxylates. One of these, amidinates, the 1,3-nitrogen analogues of carboxylates, show a rich and varied coordination to both main group and transition metals. However, the triaza analogues, substituted guanidinates, had received little or no attention as ligands prior to this work, in which the ligand chemistry of neutral, mono- and dianionic guanidines has been explored.

The synthesis and characterisation of tri-substituted guanidines containing a variety of alkyl (Pr, Bu, Cyx) and aryl (Ph, p-tol) substituents is described herein. Preparation of the homochiral substituted N,N',N''-tris((S)-(−)-ω-methylbenzyl)guanidine and the X-ray crystal structure of its PF₆ salt are also presented. In the solid state the central CN₃ unit exhibits local C₃ symmetry and has steric elements on one of the plane resulting in two stereochemically different faces. The formation of tetra-substituted N,N-diethyl-N',N''-diphenylguanidine is also detailed.

Formation of complexes containing neutral guanidine ligands was achieved in the reactions of N,N',N''-triphenylguanidine with CoCl₂ and Ag(SO₃CF₃). The complexes formed, [Co{PhN=C(NHPh)₂}₂Cl₂] and [Ag{PhN=C(NHPh)₂}₂][SO₃CF₃] respectively, were characterised by X-ray crystallography and found to contain monodentate guanidine ligands bound through their imine nitrogen alone. The cobalt complex adopts pseudo-tetrahedral geometry while [Ag{PhN=C(NHPh)₂}₂] is perfectly linear at silver with the triflate acting only as a counterion.

Cleavage reactions of the ruthenium chloro-bridged dimers [(p-cymene)RuCl₂]₂ and [Cp*RuCl₂]₂ with various tri-substituted guanidines were undertaken. Two products obtained from these reactions, namely [(p-cymene)Ru{η²-(PrN)₂CNHPr}Cl] and [Cp*Ru{(η⁶-p-tol)N=C(NHp-tol)}]⁺, were characterised by X-ray crystallography. The first of these contains a ruthenium centre with a η⁶-arene, terminal chloride and monodeprotonated chelating guanidinate ligand. Meanwhile the second is a sandwich compound in which the guanidine is bound through an arene substituent and not one of its nitrogens.
In an attempt to synthesise guanidinate complexes of early transition metals, reactions of \([\text{Ti}(\text{NMe}_2)_4]\) with guanidines were undertaken. These proved reluctant to crystallise so attention moved to the reaction of dilithiated guanidines with group IV metal halides though these products also proved difficult to characterise. In order to pre-empt the geometry and reduce the solubility of the products \([\text{MCl}_4(\text{thf})_2]\) \((\text{M} = \text{Ti, Zr})\) was reacted with monolithiated guanidines. Again a mixture of products was obtained so finally reactions with a tetra-substituted guanidine were examined as these could only be monodeprotonated. Unfortunately, single crystals suitable for X-ray diffraction were not obtained so only spectroscopic evidence was obtained for these products.

In collaboration with D.S. Wright, reactions of guanidines with the metallating agents antimony tris(dimethylamide) \([\text{Sb}(\text{NMe}_2)_3]\), tin bis(dimethylamide) \([\text{Sn}(\text{NMe}_2)_2]\) and dicyclopentadienyltin \([\text{Cp}_2\text{Sn}]\) were studied. Reaction of \(\text{N}_x\text{N'}\text{N''}-\text{tri(isopropyl)guanidine with one molar equivalent of antimony tris-dimethylamide resulted in the formation of \([\text{Sb}\{\text{Pr'N}_2\text{CNHPr'}\}\{\text{Pr'N}_2\text{CNPr'}\}]\) in which the antimony is formally chelated by monoanionic and dianionic guanidinates. The geometry of the \(\text{N}_4\text{Sb} \) unit is best described as a highly distorted trigonal-bipyramid with the residual lone pair taking up the fifth coordination site. The uncoordinated \(\text{N—H}\) on the monoanionic guanidine hydrogen bonds to an adjacent molecule and these chains form right or left handed helices. Helical structures are very rarely observed in metal complexes and the hydrogen bonded association in \([\text{Sb}\{\text{Pr'N}_2\text{CNHPr'}\}\{\text{Pr'N}_2\text{CNPr'}\}]\) is believed to be unprecedented.
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<tr>
<td>Ar</td>
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</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>cm</td>
<td>complex multiplet</td>
</tr>
<tr>
<td>cod</td>
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</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
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</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>δ</td>
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</tr>
<tr>
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</tr>
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<td>acetonitrile</td>
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<tr>
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</tr>
<tr>
<td>Otf</td>
<td>trifluoromethanesulphonate, triflate</td>
</tr>
<tr>
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<td>quartet</td>
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<td>singlet</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
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</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
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<td>Thin Layer Chromatography</td>
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<tr>
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<td>trimethylenemethane</td>
</tr>
<tr>
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CHAPTER ONE

INTRODUCTION

The use of asymmetric catalysis to produce enantiomerically pure compounds is, at present, a huge growth area within the chemical industry. One particular facet of this is the development and application of metal based homogeneous catalysts. Catalytic systems of this type are employed primarily in the synthesis of biologically active materials, such as pharmaceuticals and agrochemicals, in which enantiomeric purity is often essential. The economic gains from using catalytic over stoichiometric processes result from the reduction of expensive chiral material that has to be used as one chiral catalyst molecule can produce many chiral product molecules. Also, as the selectivity of homogeneous systems is generally very high, there is no reduction of yield in the process due to the formation of an unwanted enantiomer. The optimisation of these catalyst systems results from the design of the chiral ligands. Research and development of new ligand systems holds the key for the future improvement and expansion of the use of homogeneous catalysis.

At present there are a large number of different ligand systems which are utilised in asymmetric catalysis. In the case of hydrogenation the majority of these ligands are bidentate, e.g. $C_2$-symmetric diphosphines, which upon coordination to a metal in a square planar environment form $C_2$-symmetric complexes (Fig. 1.1a). These systems are highly efficient asymmetric catalysts because the remaining

![Figure 1.1. Conformations at metal centres.](image)

Figure 1.1. Conformations at metal centres.
coordination sites available to a substrate (A&B) are homotopic. However, employment of \( C_2 \)-symmetric ligands with octahedral complexes is not as efficient as two diastereotopic environments are available for substrate binding (Fig. 1.1b). However, upon coordination of a chiral tridentate ligand to the face of an octahedral complex, a \( C_3 \)-symmetric complex results in which the three remaining coordination sites are all homotopic (Fig. 1.1c). For this system only one possible substrate bound transition state can exist which should, therefore, result in high enantiomeric yields of products. The synthesis and characterisation of new, chiral tridentate ligand systems was the initial focus of this work.

The ligand systems chosen for study were based on the trimethylenemethane dianion (TMM\(^2^-\)) which is well known to act as a tridentate ligand after it was first reported. A series of anionic species isoelectronic to TMM\(^2^-\) exists which includes the common ligands carbonate, nitrate and the less well studied nitrogen analogue guanidinates. Unlike the other members of the series, the ligand chemistry of guanidinates (and in particular its trisubstituted derivatives) had received little attention, and it is these compounds which have been investigated as ligands within this thesis.

Having introduced some of the reasons for studying these ligand systems it is now proposed to survey and discuss the published research relevant to this field of work.

1.1 Trimethylenemethane Metal Complexes

In 1966 Emerson et al reported the preparation of the first trimethylenemethane (TMM) metal complex which was derived from the reaction between diiron nonacarbonyl and 3-chloro-(2-chloromethyl)propene (Fig. 1.2).\(^{(1-3)}\)

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Fe}_2(\text{CO})_9 & \quad \rightarrow \quad \text{Fe} \quad \text{CO} \\
\text{OC} & \quad \text{Fe} \quad \text{CO} \\
\text{FeCl}_2 & \quad \text{OC}
\end{align*}
\]

*Figure 1.2. Synthesis of Fe(tmm)(CO)\(_3\).*
The stable complex was characterised by elemental analysis, IR, mass and NMR spectroscopy. The discovery that the π-type TMM dianion coordinated in the \( \eta^3 \) mode as a 6π electron donor was unique at that time and further work by Emerson et al lead to more iron TMM complexes via the dehydrohalogenation of suitable allyl complexes, e.g. [Fe(CO)\(_3\)Cl(\( \eta^1\)-C\(_4\)H\(_7\))]\(^{(1-4)}\). Their continued study of these complexes turned to the synthesis of substituted trimethylenemethane complexes\(^{(1-5)}\). Various alkyl, aryl, alkoxy and halogeno substituted TMM complexes were successfully synthesised, all of which were found to be highly coloured and air stable. Spectroscopic characterisations determined that stronger backbonding occurred for the TMM complexes when compared with the analogous diene complexes. However, as the complexes were all volatile liquids crystallographic data for the complexes proved elusive.

The field of TMM ligand chemistry was opened up by the discovery of functionalised allyl silane derivatives as ligand transfer reagents (Fig. 1.3)\(^{(1-6)}\). This led to a large number of TMM complexes of the late transition metals initially iridium, osmium, rhodium and the first isolated example of a ruthenium TMM complex, [RuCl(NO)(PPh\(_3\))(TMM)]\(^{(1-6)}\). Herberich and Spaniol successfully developed the use of bistrimethylstannyl derivatives as ligand transfer reagents in the synthesis of yet more TMM complexes of transition metals\(^{(1-7)}\). Using this method they were able to synthesise the ruthenium tricarbonyl TMM complex analogous to [Fe(CO)\(_3\)(TMM)].

1.2 THE TRIMETHYLENEMETHANE DIANION AND ISOELECTRONIC SYSTEMS

The structure and bonding of the trimethylenemethane dianion (TMM\(^2^-\)) has been a subject of intense debate in the chemical literature. The ready deprotonation of isobutylene to TMM\(^2^-\) occurs in a two step process in which the intermediate allyl anion is deprotonated more rapidly than the neutral starting material (Fig. 1.4).\(^{(1-8)}\) This indicates that there is some unusual electronic stability associated with the
Chaper One

Introduction

dianion and initial arguments\(^{(1-9)}\) suggested the possibility of “aromatic” delocalisation of the six \(\pi\)-electrons over the structure. It has since been suggested that the stability is electrostatic in origin with the attraction of the central tricoordinate positive carbon and the three negative methylenes accounting for the stability.\(^{(1-10)}\)

A large number of stable Y-shaped systems isoelectronic to TMM\(^{2-}\) are known (Fig. 1.5).\(^{(1-9)}\) These include the common anions nitrate and carbonate and even the boron trihalides may be considered in this way. A variety of other less common species are also known to exhibit remarkable thermodynamic stability.

\[
\begin{align*}
\text{Figure 1.4. Stepwise deprotonation of isobutylene.}
\end{align*}
\]

\[
\text{Figure 1.5. Isoelectronic Y-shaped systems.}
\]

This stability is typified by guanidine \([(NH_2)_2C=NH]\) which is the strongest known organic base \((pK_a = 13.6)\), approaching hydroxide in its proton affinity. Upon protonation the resulting six \(\pi\)-electron carbonium ion is found to be inert to boiling water making it the most stable carbonium ion known.\(^{(1-9)}\)

Many of the ions in this series behave as ligands towards both transition and main group metals. Previously, the oxoanions nitrate\(^{(1-11)}\) and carbonate\(^{(1-12)}\) were known to coordinate as simple Lewis bases through their lone pairs and form mono- and bidentate complexes. It is for this reason that the discovery of the \(\eta^3\)-facial coordination mode of the TMM ligand generated interest in this field.

The replacement of methylenes by combinations of O, NR, S or SiR\(_2\) to form heterotrimethylenemethanes [C(XYZ)]\(^n\) leads to new mono- and dianions which are potential six electron donors (Fig. 1.6). The presence of these stronger donor atoms suggests that heterotrimethylenemethanes would show preferential coordination to more electropositive metals (early transition, main group). However,
TMM is known to exhibit π-acidity as a ligand so the heteroTMM ligands may also coordinate to the later transition metals depending on the electronic structure of the individual ligands. Interconversion of heteroatoms has the potential to provide a source of ligands with potentially fine-tuneable stereoelectronic properties.

A number of these potential ligands have already been studied and were found to coordinate to transition metals in both $\eta^1$ and $\eta^2$ modes. However, the triaza ligands, guanidine dianions (which bear the same relationship to carbonic acid as amidines and triazines do to carboxylic acids), had received little attention and have only recently featured to any great extent in the chemical literature. This is in contrast to the isoelectronic carbonate\(^{(1-12)}\) and the isostructural 1,3-nitrogen anions of amidines\(^{(1-13)}\) and triazines\(^{(1-14)}\) which have both been widely studied as ligands and show a rich and varied coordination to both main group and transition metals.

### 1.3 GUANIDINES

The double deprotonation of guanidine to yield the Y-shaped triazatrimethylenemethane dianion (TAM\(^2^-\)) results in a species isoelectronic to TMM\(^2^-\). The isoelectronic nature of these to carbonates and the superior ability of nitrogen to act as a donor ligand to transition metals would indicate that the coordination of guanidines to transition metals could be readily accomplished. Very few complexes containing dianionic guanidine ligands are known, though a number containing neutral or monoanionic guanidine ligands have been reported, the majority of these featuring unsubstituted or tetramethyl guanidine. However, with the aim of this thesis being the synthesis of \(C_3\)-symmetric complexes, trisubstituted guanidines were synthesised with the hope that, upon $\eta^3$ coordination to a metal centre, the guanidine substituents will adopt either a clockwise or anticlockwise conformation yielding \(C_3\)-symmetric complexes (Fig. 1.7).

![Figure 1.7. Trisubstituted guanidine and formation of \(C_3\)-symmetric complex.](image)
A short review of guanidine ligand chemistry by Mehrota was published in *Comprehensive Coordination Chemistry*. This gave an introduction to the various aspects of the field, which at the time of writing was dominated by reports of guanidinium cations (binding to anions) and neutral guanidines forming adducts though the imine nitrogen. However, in the past decade the coordination of deprotonated guanidines (guanidinates) to metals has received more attention and the volume of work reported in this area has blossomed.

A variety of complexes formed by ligands containing the guanidine moiety are reported in the chemical literature. A vast number of these reports detail complexes in which guanidinium cations are present, but these are not present in the coordination sphere of the metal ion and are consequently merely present as counterions. Cyanoguanidines have also received a great deal of attention but in the main they are coordinated to the metal through the cyano nitrogen alone and the guanidine moiety plays no part in metal binding. The bioligands creatine and creatinine, which contain guanidine moieties, have a rich and varied coordination chemistry which was reviewed recently by Mitewa. Furthermore, a discussion of the synthesis and chemistry of guanidine derivatives was published by Yamamoto and Kojima. This also contains some information on the coordination of guanidines to anions and crown ethers.

However, this thesis is primarily concerned with the ability of guanidine molecules and their deprotonated anions to coordinate to metal centres. As a consequence only complexes in which the guanidine moiety is directly bound to the metal (i.e. through a nitrogen of the central CN$_3$ core) are considered in this review of previous work in the field.

### 1.4 Complexes Containing Neutral Guanidines

There are a large number of complexes reported which contain a neutral guanidine ligand and these can be classified into two main groups:

(i) substituted guanidines containing no additional donor atoms and

(ii) substituted guanidines containing additional donor atoms.
The major difference in the coordination chemistry of these classes is that when no additional donor atoms are present, the guanidines act exclusively as monodentate ligands binding through the lone pair located on the imine nitrogen. However, when additional donor atoms are present there is a tendency for the molecules to behave as bidentate ligands. For this reason, and also to emphasise the coordination of the guanidine moiety, these two classes will be reviewed in separate sections.

1.4.1 With No Additional Donor Atoms

The early reports of complexes of this type focused on the formation of adducts with 1,1,3,3-tetramethylguanidine [tmg; HNC{N(CH$_3$)$_2$}$_2$] and to date the majority of known complexes containing a neutral guanidine contain this ligand. The first report of complexes containing this ligand (indeed the first report of a guanidine coordinating to a metal) was published by Drago et al in 1965.$^{1-20}$ Complexes of Co(II), Cu(II), Zn(II), Pd(II), Ni(II) and Cr(III) were prepared with the tetracoordinate cobalt, copper, and zinc perchlorate complexes characterised by spectroscopy, magnetic measurements and X-ray powder diffraction. Elemental analyses confirmed that these complexes had the composition [M(tmg)$_4$(ClO$_4$)$_2$]. A shift towards lower wavenumbers {e.g. from 1609 to 1548 cm$^{-1}$} in [Co(tmg)$_4$(ClO$_4$)$_2$] of the $\nu$(C=N) stretch in the IR spectrum confirmed coordination through the imine nitrogen. The cobalt complex was suggested to have a tetrahedral geometry based on spectral and magnetic measurements although this could not be confirmed from X-ray powder diffraction data. The copper and zinc complexes were also found to have tetrahedral geometries and their X-ray powder patterns were very similar suggesting that they showed little distortion from true tetrahedral symmetry.

As part of their study of the interaction of imines with aluminium Lewis acids, Wade et al examined the adduct formation of tetramethylguanidine with AlX$_3$ (X = Me, Et, Cl).$^{1-21}$ The 1:1 reaction of these produced the adducts [(Me$_2$N)$_2$CNH•AlX$_3$] which were found to be monomeric in benzene. Infra-red and $^1$H NMR spectroscopy of the adducts confirmed that the guanidine binds through the
imine nitrogen (Fig. 1.8). Thermal decomposition of the alkyl aluminium adducts led to evolution of alkane (RH) leaving dialkyl-(diaminomethyleneamino)aluminium which contains a monoanionic guanidinate ligand. These were found to exist as dimers in benzene (by cryoscopy) and $^1$H NMR data suggests that the guanidinate ligands are bridged by dialkyaluminium groups (Fig. 1.8). The analogous dichloro complexes were prepared from the reaction of the monolithiated guanidine [(Me$_2$N)$_2$C=NLi] and AlCl$_3$.

The reaction of guanidines with [Pt(trpy)Cl]$^+$ (trpy = 2,2'-6',2''-terpyridine) was reported by Kostic et al as part of their efforts to model the metal binding sites in metallo-proteins.$^{1-22}$ The product complex, characterised by UV-Vis and IR spectroscopy, contains a square planar Pt(II) centre coordinated by a tridentate trpy ligand and a monodentate guanidine, binding through its imine nitrogen (Fig. 1.9). A range of monosubstituted guanidines were studied from methylguanidine to the biomolecules arginine, N-acetylarginine and canavanine [where R = -{(CH$_2$)$_3$CH(NH$_3$)(COO)}, -{(CH$_2$)$_3$CH[CH$_3$C(O)NH](COO)} and -{O(CH$_2$)$_2$CH(NH$_3$)(COO)} respectively].

This communication was followed by a report describing the first crystallographic study of a guanidine binding to a transition metal.$^{1-23}$ The synthesis of bimetallic complexes, where the guanidine bridges the metals, was achieved by the 2:1 reaction of the appropriate guanidine hydrochloride with the Pt(trpy) fragment in aqueous solution. A similar range of substituted guanidines were studied and the structure of the bimetallic complex [{Pt(trpy)}$_2$(can)]$^{3+}$ (where can = canavanine) was determined by X-ray diffraction (Fig. 1.10). In this case the
canavanine ligand is anionic though the negative charge resides solely on the carboxylate which plays no part in metal binding. Hence, no charge resides on the guanidine moiety and it can be considered as a neutral bidentate donor. In the crystal structure the two Pt(trpy) fragments are bridged by the guanidine ligand giving a Pt-Pt distance of 2.9884(7) Å. The trpy groups are almost parallel [angle between the planes is approximately 9°] and are nearly eclipsed with each other. The Pt-N distances are similar [Pt(1)-N(4) 2.06(1) Å and Pt(2)-N(8) 2.07(1) Å] and the CN₃ core of the guanidine remains planar. One C-N distance remains considerably shorter than the other two [1.26(2) Å vs. 1.34(2) and 1.36(2) Å] confirming the presence of a double bond and the neutrality of the guanidine function.

Davison et al., reported the formation of a monodentate 1,1,3,3-tetramethylguanidine complex upon reaction of 2,3,5,6-tetramethylbenzenethiolate (tmbt) with the technetium nitridotetrachloride anion [TcNCI₄]⁻ in the presence of tetramethylguanidine.¹²⁴ The formation of a guanidine complex was somewhat fortuitous as the anticipated product was [TcN(tmbt)₂] and tetramethylguanidine was only present in the reaction mixture as a "noncoordinating" base. The isolated product [TcN(tmbt)₂(tmg)₂] has equivalent ¹H NMR signals for the tmbt and tmg ligands, which suggests that the ligands are bound in a transoid fashion across the base of a square pyramid. This was confirmed by an X-ray crystal structure study (Fig. 1.11). The nitrido group is in the apical position with the other ligands alternating around the square base. The guanidine ligands are symmetrically bound to the technetium through their imine nitrogens [Tc(1)-N(3) 2.130(6) Å and
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Tc(1)-N(4) 2.128(6) Å with the dimethylamino nitrogens uncoordinated. The guanidines are indeed neutral ligands as hydrogens were located on both the imine nitrogens from Fourier difference maps and further evidence was supplied from the 1H NMR spectrum which shows a signal for 2H at 3.87 ppm.

Another complex containing a monodentate, tetrasubstituted guanidine ligand was obtained from the reaction of diiodobis(N-isocyanodialkylamine)platinum(II) with excess dialkylamine. The products, [PtI₂(HNR₂){HN=C(NR₂)₂}] (where R = Et, 2R = -(CH₂)₅-, -(CH₂)₂O(CH₂)₂-), were spectroscopically characterised and, where R = Et, by X-ray diffraction. From the IR spectra, ν(C-N) was found at 1512 cm⁻¹, approximately 100 cm⁻¹ lower than would be expected for the free guanidine and indicative of the guanidine binding through the imine nitrogen. The 1H NMR spectrum shows two signals for N-H protons confirming that the guanidine is indeed neutral. In the crystal structure of [PtI₂(HNET₂){HN=C(NET₂)₂}] (Fig. 1.12), the platinum has square planar geometry [I-Pt-N 89-93°] with the nitrogen ligands coordinated trans to each other. The iodine atoms are coordinated symmetrically [Pt-I(1) = Pt-I(2) = 2.597(2) Å] though the Pt-N bond lengths are slightly different. The guanidine coordinate bond is shorter than that for the amine [Pt-N(1) 2.006(9) Å and Pt-N(2) 2.095(9) Å] which would be expected as the guanidine is bound via a sp² hybridised imine nitrogen. The central CN₃ core of the guanidine is planar though as a result of coordination the imine bond is slightly lengthened [C(1)-N(1) 1.32(1) Å; c.f. 1.36(1) and 1.35(2) Å for C(1)-N(3) and C(1)-N(4) respectively]. It was suggested that this may also be as a result of resonance within the CN₃ core.

A recent report from Schmidbaur et al detailed the first guanidine complexes of gold(I). The high yielding, stoichiometric reactions between tetramethylguanidine and [AuCl(SMe₂)] or [AuBr(tht)] (tht = tetrahydrothiophene) gave [(tmg)AuCl] and [(tmg)AuBr] respectively. In

![Figure 1.12.](image)

![Figure 1.13.](image)
solution these were found to exist in equilibrium, in which the ligands exchange to form molecular and ionic species (Fig. 1.13). However, the crystalline precipitates of these mixtures show single $\nu$(NH) and $\nu$(C=N) bands in their IR spectra indicating that they are of uniform composition. X-ray crystallography confirmed that they exist in the ionic form (Fig. 1.14). The $[\text{Au\{NH=C(NMe}_2\}_2\}]^+$ cations and $\text{AuBr}_2^-$ anions form ion pairs via Au⋯Au contacts [3.1413(8) Å]. Both the axes N(1)-Au(1)-N(4) and Br(1)-Au(2)-Br(2) are virtually linear [178.8(5)$^\circ$ and 176.89(6)$^\circ$ respectively]. These units enclose a dihedral angle of 41.5$^\circ$ and this precludes any hydrogen bonding between the NH and Br groups. In the cation, the two coordinate bonds are equal within one standard deviation [Au(1)-N(1) 2.006(9) Å, Au(1)-N(4) 1.993(9) Å]. The guanidine is bound to the metal through its imine nitrogen with the amine (NMe$_2$) groups not involved in coordination.

The other guanidine complex reported in the paper was formed by the reaction of tetramethylguanidine with $[(\text{Ph}_3\text{P})\text{Au(OTf)}]$ to yield $[\text{Au\{NH=C(NMe}_2\}_2\}\text{(PPh}_3\text{)}]^+(\text{CF}_3\text{SO}_3)^-$, the structure of which was also determined (Fig. 1.15). The P(1)-Au(1)-N(1) axis is slightly distorted from linear [177.1(3)$^\circ$] and the guanidine is again coordinated through its imine nitrogen, though the coordinate bond is slightly longer than the previous example [Au(1)-N(1) 2.044(9) Å]. Of the three C-N distances the imine bond is shorter than the others [C(1)-N(1) 1.27(1) Å c.f. C(1)-N(2) 1.32(1) Å and C(1)-N(3) 1.38(1) Å] although all three are intermediate between single and double bonds. This, allied to the fact that the central CN$_3$ unit is planar (sum of angles total 360$^\circ$), would indicate that there is extensive delocalisation over the guanidine ligand.

A final example of neutral guanidine coordination was described by Mitewa et al.$^{(1-27)}$ Reaction of two or four molar equivalents of triphenylguanidine with
(NH₄)₂[PdCl₄] in aqueous methanol yields the complexes [Pd{(PhN)C(NHPh)₂}₂Cl₂] and [Pd{(PhN)C(NHPh)₂}₄](ClO₄)₂. In their IR spectra these both exhibit a reduction in ν(C=N) from the free ligand, indicative of coordination through the imine nitrogen. A crystal structure determination was performed on the bis-guanidine complex (Fig. 1.16). The complex has distorted square planar geometry around the Pd [angles in the range 88.77(20) - 91.63(20)°] with the ligands trans around the Pd centre. The guanidines are symmetrically bound to the metal [Pd-N(11) 2.036(7) Å and Pd-N(21) 2.023(7) Å] and coordination through the imine nitrogen is confirmed by analysis of the C-N distances within the central CN₃ unit [C(11)-N(11) 1.309(11) Å and C(21)-N(21) 1.312(11) Å; c.f. range 1.348(11) - 1.364(11) Å for the non-coordinating nitrogens]. Two of the amine hydrogens [H(13) and H(23)] form hydrogen bonds of the type N-H⋯Cl to the chloride ligands. These bonds range from 3.409(8) to 3.317(7) Å and the N-H-Cl angles from 139(1) to 144(1)°.

All of these complexes show that a neutral guanidine, with no additional donor atoms, will coordinate as a monodentate ligand through the imine nitrogen alone. A feature of these ligands is that upon coordination the central CN₃ core remains planar and the C-N distances become intermediate between single and double bonds. This is indicative of the extensive delocalisation that exists within the guanidine ligand and the delocalisation may also enhance the inherent stability of these complexes.
1.4.2 WITH ADDITIONAL DONOR ATOMS

1.4.2.1 CYANOGLANIDINES

There is large scope for the introduction of different substituents (which may contain additional donor atoms) onto a guanidine moiety, as their stepwise synthesis readily permits the incorporation and variation of substituent groups. The most commonly encountered example which contains an additional donor atom is cyanoguanidine.

Complexes containing cyanoguanidine \{\text{cng}; (\text{NH}_2)_2\text{CNCN}\} ligands are fairly common in the literature although in the majority of cases it acts as a monodentate ligand, binding to the metal through the cyano nitrogen alone. However, examples in which any of the guanidine nitrogens are actually involved in metal coordination are scarce. In these few examples the cyanoguanidine is invariably found to act as a bidentate, bridging ligand coordinated to two separate metal centres via the nitrile nitrogen and the imine nitrogen to which the nitrile is bonded. The major differences between these complexes arise in the way the metal-guanidine units interact with each other to form either dimers or oligomeric structures. This in turn, is normally due to the steric effects imposed on the complexes by the coordination geometry at the metal centre or by the other ligands which are bound to the metal rather than any steric or electronic influence that the cyanoguanidine ligand exerts.

The first structurally characterised cyanoguanidine complex was obtained from the reaction of ethylenediamine hydrochloride, cyanoguanidine and copper(II) sulphate.\(^{1-21}\) The isolated crystals analysed as the anticipated product ethylenebisbiguanidecopper(II) sulphate except for the presence of a C≡N stretch in the IR spectrum. The structure was determined as 1-(2-aminoethyl)biguanidecyanoguanidinecopper(II) sulphate monohydrate by an X-ray diffraction study.
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Of the large number of complexes containing cyanoguanidine ligands synthesised by Hubberstey et al only four show direct coordination of the imino nitrogen of the guanidine moiety. In di-µ-sulphato[tetra-aquabis-µ-cyanoguanidinedicadmium(II)] (Fig. 1.17) the two cadmium atoms are bridged by the two cyanoguanidine ligands; one cadmium bound to the cyano nitrogen N(1), the other to the imino nitrogen N(2). The remaining amino nitrogens of the guanidine play no part in coordination to the cadmium. The two water molecules are trans to these Cd-N bonds with the sulphato groups occupying the axial positions. The Cd₂(cnge)₂ units are essentially planar and these planes are linked together by bridging sulphato anions to form infinite chain structures.

Reduction of copper(II) chloride in the presence of cyanoguanidine yields [Cu₂(cnge)₄]²⁺ where the cyanoguanidine again acts as a bidentate bridging ligand (Fig. 1.18). The copper(I) centres are bridged by two cyanoguanidine ligands to form an eight membered metallacycle [Cu-N C-N-Cu-N C-N]. The coordination mode of the cyanoguanidine is similar to the previous example in that the nitrilic nitrogen N(1) and the imino nitrogen N(3) form coordinate bonds to the metals with the amino nitrogens [N(5) & N(6)] uncoordinated. The distorted trigonal planar geometry of the copper(I) centres is completed by a second molecule of cyanoguanidine which binds, in a monodentate manner, through its nitrilic nitrogen N(7). In contrast to the previous example though, no other ligands are bound to the metal leaving the copper(I) centres coordinatively unsaturated. In the solid phase, the
dimeric units stack in a lattice such that the nitrile function of a monodentate cyanoguanidine ligand is in the axial position of a neighbouring Cu(I) atom.

Further examples of cyanoguanidine acting as a bridging ligand were reported by Hubberstey et al in 1994.\(^{(1,31)}\) This report again describes the reduction of copper(II) halides in the presence of cyanoguanidine to yield the complexes \([\text{Cu}_2\text{X}_2\text{cnge}]\) (X = Cl or Br) and \([\text{CuBr-cnge-H}_2\text{O}]\). However in this case, due to the coordination of residual halides, the Cu(I) centres are more sterically hindered so dimers are not able to form. Instead the \([\text{XCu(cnge)}]\) units form chains in the solid state (Fig. 1.19). Once again the cyanoguanidine is bound through its nitrilic N(1) and imino N(2) nitrogens with the amino nitrogens [N(3) & N(4)] uncoordinated.

A further example of a bridging cyanoguanidine ligand is found in the complex \([\text{Hg(cnge)Cl}_2]\) reported by Pickardt et al.\(^{(1,32)}\) The mercury atoms have an octahedral geometry with four chlorine atoms in equatorial positions and two cyanoguanidine nitrogens in the axial sites (Fig. 1.20). The Hg atoms are bridged by two chlorine atoms and these HgCl\(_2\) units form polymeric chains. These chains are cross linked by bidentate bridging cyanoguanidine ligands to form a net-like array. The cyanoguanidine is again bound to the metal through the cyano N(1) and imino N(2) nitrogens.

1.4.2.2 AZO AND PHOSPHOROUS SUBSTITUTED GUANIDINES

Incorporation into the guanidine of donor atoms/groups other than nitrile also usually results in the guanidine acting as a bidentate ligand. The ligand normally binds through one of the guanidine nitrogens and the other donor atom although it is also known for the metal to be bound by two of the guanidine nitrogens.
The ligand pyridine-2-azo-p-phenyltetramethylguanidine (PAPT) (Fig. 1.21) was synthesised and its interactions with \( \text{Ni}^{2+}, \text{Co}^{2+} \) and \( \text{Zn}^{2+} \) were studied.\(^{1-33}\) These reactions were followed by UV-Vis spectroscopy and the ligand was found to chelate to the metals. Complexation of the first equivalent of metal occurred through the azopyridine nitrogens and the second equivalent through the imine and amine nitrogens of the guanidine moiety.

A further report of the PAPT ligand detailed its complexation of lithium cations.\(^{1-34}\) The paper also reports the reactions of 4,4'-bis(tetramethylguanidine)azobenzene (BTA) (Fig. 1.21). For both ligands, dimers were formed with the \( \text{Li}^+ \) bridging between either a pyridyl nitrogen and an imine nitrogen (PAPT) or between two imine nitrogens (BTA).

A different type of substituted guanidine, guanidinopyrimidine, which contains an additional donor nitrogen, was studied by Zawadski et al.\(^{1-35} \) 2,6-dichloro-4-guanidinopyrimidine and 4,6-dichloro-4-guanidinopyrimidine were utilised as potential chelating ligands in reactions with Pd(II) salts. Upon chelation, shifts in the stretching frequencies in the guanidine and pyrimidine moieties were observed in the IR spectrum, suggesting coordination through both groups. UV-Vis spectroscopic analysis agreed with this postulation and a proposed structure of the complexes has the Pd coordinated by the imine nitrogen from the guanidine and one of the pyrimidine nitrogens (Fig. 1.22).
The reaction of methanol with the cyanoguanidine complex [Pt(cnge)$_2$(PPh$_3$)$_2$][BPh$_4$]$_2$ (in which the cyanoguanidine is bound through its cyano nitrogen alone) in acetone solution provided the unusual azametallacyclic species cis-[(Ph$_3$P)$_2$Pt{NHC(OMe)=NC(NH$_2$)=NH}][BPh$_4$]. The structure of the azametallacycle was confirmed by X-ray crystallography and was shown to contain a bidentate ligand binding through guanidine and cyano nitrogen atoms (Fig. 1.23). This ligand forms as a result of activation, by the Pt(II) centre, of a cyanoguanidine ligand towards nucleophilic addition of MeOH at the cyano group and deprotonation of the guanidine group. In the crystal structure itself, the platinum ion exhibits square planar geometry, bound by two phosphines and the azametallacycle. The six-membered chelate ring is planar indicating a delocalised π-electron system and the two coordinate bonds are essentially identical [Pt-N(1) 2.048(6) Å and Pt-N(2) 2.032(7) Å].

Complexes of phosphorylguanidines, where the ligand binds through a guanidine nitrogen and the phosphoryl oxygen, were reported by Lin et al. The reaction of dialkylphosphorylguanidines with metal ions was followed by UV titration and conductivity measurements and evidence for complex formation was obtained with Cu$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, Ni$^{2+}$ and Al$^{3+}$. It was found that the free ligands undergo an intramolecular rearrangement to yield, in the solid state, a six-membered structure containing an intramolecular hydrogen bonding bridge (Fig. 1.24).
Complexes of phosphorous substituted tetramethylguanidine have been reported recently by the group of Schmutzler. The first of these papers discusses the reactions of dialkylphosphinous-\( \text{N}(N',N'',N''',N''''\text{-tetramethyl})\text{guanidines and alkylphosphonous-bis-}N(N',N'',N''',N''''\text{-tetramethyl})\text{guanidines with zerovalent transition metals.}^{(1-38)}\) Mostly the ligands bound through the phosphorous alone though reaction with tetracarbonyl molybdenum fragments produced complexes containing PN- and PNN'-donor ligands which were characterised by IR and NMR spectroscopy (Fig. 1.25).

![Figure 1.25.](image)

A second paper from this group reported the reaction of alkylphosphonic-bis- \( \text{N}(N',N'',N''',N''''\text{-tetramethyl})\text{guanidine with a variety of first row transition metals.}^{(1-39)}\) Again coordination through the P=O bond is observed though coordination through guanidine nitrogens is also observed. In fact for the complex \([('BuP=O)(tmg)_2\cdot\text{CuCl}_2]\) the ligand chelates the metal binding through guanidine imine nitrogens alone. Chelation of the metal forms a four-membered Cu-N-P-N metallacycle which is slightly puckered [7.9° along 'N(1)-N(4) axis]. The copper atom has distorted square planar geometry, the largest deviation occurring for the endocyclic angle N(1)-Cu-N(4) 72.68(9)°, due to the restricted bite of the ligand. The ligand symmetrically binds the copper \([\text{Cu-N(1)} 200.6(3) \text{ pm, Cu-N(4)} 200.4(2) \text{ pm}]\) through its imine nitrogens, the amine (NMe₂) groups remaining uncoordinated.
These articles show that the attachment of additional donor atoms onto the guanidine moiety can have a marked effect on its ligand capabilities. Although at present there are only a handful of reports of ligands of this type, a diversity in binding mode of the ligands already exists. From these few reports it seems clear that a large, and as yet unexplored, area of coordination chemistry exists and that many novel ligand systems, based on substituted guanidines, show promise for future research in this field.

1.5 Complexes Containing Monoanionic Guanidines

Reports of complexes containing a monoanionic guanidine (guanidinate) ligand were very scarce until the beginning of the decade. Since then however, interest in these ligands has surged and a number of accounts of novel complexes have been published. The guanidinate ligand is found to exist in a number of different coordination geometries as a chelating or bridging ligand binding through one, two or three nitrogen atoms.

1.5.1 Chelating Guanidinate Ligands

The first report of monoanionic chelating guanidinate complexes was published by Bailey et al. Treatment of the chloro-bridged dimers, [Cp*RhCl₂]₂ and [(p-cymene)RuCl₂]₂, with four molar equivalents of 1,2,3-triphenylguanidine in toluene solution led to precipitation of two equivalents of the guanidinium chloride salt leaving the chelate complexes [Cp*Rh{η²-(PhN)₂CNHPh}Cl] and [(p-cymene)Ru{η²-(PhN)₂CNHPh}Cl] in solution. In this case two equivalents of the guanidine act as a base and also a halide abstractor, removing a proton from the other guanidine equivalents and a halide from the metal. The structures of the complexes were determined by X-ray diffraction and were found to be very similar with the metal ligated by a η-bonded aromatic, a terminal chloride and a chelating triphenylguanidinate. In the rhodium complex (Fig. 1.26) the coordinate bonds are slightly different [Rh-N(1B) 2.085(6) Å, Rh-N(1C) 2.136(8) Å] though this may be
due to steric repulsion between the phenyl substituents on N(1B) and N(1C) rather than an actual difference in their donor strengths. Within the guanidine moiety the central CN$_3$ unit is planar and the C-N distances show no double bond character, indicating a delocalisation of charge within this group. Although the amine hydrogen was not located in the structure, $^1$H and $^{13}$C NMR showed the phenyls to be in a 2:1 ratio, consistent with the N-H being on the uncoordinated nitrogen.

N,N'-diphenylguanidine was found to react with the transition metal hydrides [MH$_2$(CO)(PPh$_3$)$_3$] (M = Ru, Os) yielding complexes containing chelating monoanionic guanidine ligands.$^{(1-4)}$ The products of these reactions [MH{$^\eta^2$-PhNC(NH$_2$)NPh}(CO)(PPh$_3$)$_2$], characterised by IR and NMR spectroscopy, were found to contain mutually trans phosphine ligands with the guanidinate ligand coordinated symmetrically to the metal centre (Fig. 1.27a). In an analogous reaction [IrH$_2${$^\eta^2$-PhNC(NH$_2$)NPh}(PPh$_3$)$_2$] was obtained from [IrH$_3$(PPh$_3$)$_3$] and N,N'-diphenylguanidine (Fig. 1.27b).

Also reported was the formation of complexes containing both monoanionic and neutral guanidines in which the monoanionic guanidinate chelates the metal and the neutral guanidine acts as a monodentate ligand (Fig. 1.27c). These were synthesised in the reaction of the trifluoroacetate complexes [M(O$_2$CCF$_3$)$_2$(CO)(PPh$_3$)$_2$] (M = Ru, Os) with N,N'-diphenylguanidine. The tentative formulation of these complexes as the salts [M{$^\eta^2$-PhNC(NH$_2$)NPh}$_{\text{salt}}$].
PhNC(NH$_2$)NHPh][(CO)(PPh$_3$)$_2$][O$_2$CCF$_3$] was consistent with elemental analysis and spectroscopic data.

In a recent article Kilner et al described a number of reactions of di- and triphenylguanidine with [CpMo(CO)$_3$Cl].$^{(1-42)}$ The ability of guanidine to act as a base and a halide abstractor was also observed in the reaction between [CpMo(CO)$_3$Cl] and di- or triphenylguanidine. Displacement of a carbonyl group by the guanidine, followed by elimination of HCl (which is removed by the second guanidine to form guanidinium chloride) results in the complexes [CpMo{PhNC(NH)$_R$}NHPh](CO)$_2$] (R = H, Ph), the structures of which were determined by X-ray diffraction (Fig. 1.28, R = H). Both complexes have very similar structures, the presence of the additional phenyl group having only a limited effect on the complex as a whole. In the diphenylguanidinate complex the ligand chelates the Mo centre symmetrically [Mo-N(1) 2.187(3) Å] and with the triphenyl ligand the Mo-N distances are crystallographically equivalent [Mo-N(1) 2.172(4) Å, Mo-N(2) 2.191(4) Å]. In both complexes the central CN$_3$ units of the guanidines are planar and the bond lengths in the chelating NCN moiety are all similar [range 1.327(6) Å - 1.336(6) Å]. One difference the introduction of the phenyl ring makes is to lengthen the bond between the uncoordinated nitrogen and the central carbon [from 1.357(6) Å to 1.387(6) Å]. This is due to the bulky phenyl group causing a twist around the C-N bond which disrupts the π delocalisation in the guanidinate ligand. Hydrogen bonds form in the solid state between NH groups on the uncoordinated nitrogen and the chelating nitrogens (diphenyl ligand) or the carbonyl oxygen (triphenyl ligand).
The insertion reactions of carbodiimides into the M-N bonds of metal amides, followed by migration of the amide from the metal to the \( sp \) carbon of the carbodiimide to form chelating guanidinate anions have been reported recently by Chang and co-workers. In the first of these reports the reaction of bis(diisopropylamido)magnesium with one and two molar equivalents of 1,3-diisopropylcarbodiimide was described.\(^{(1,43)}\) The product of the equimolar reaction was characterised spectroscopically and found to be the unsolvated dinuclear complex \( [\text{Mg}_2(\mu-\text{NPri}_2)_2\{(\text{Pr}^\text{t}N)_2\text{CNPri}_2\}]_2 \) which contains chelating tetraisopropylguanidinate ligands. The 2:1 (carbodiimide to metal) reaction yielded the solvated monomer \( [\text{Mg}\{(\text{Pr}^\text{t}N)_2\text{CNPri}_2\}_2(\text{thf})] \), the structure of which was determined by X-ray crystallography (Fig. 1.29). The complex is square-pyramidal at Mg with the chelating tetraisopropylguanidinate ligands forming the basal plane and thf in the axial position. A crystallographic \( C_2 \) axis exists through the Mg-O bond making the guanidinate ligands equivalent. The metal-ligand bonds [Mg-N(1) 2.066(7) Å, Mg-N(2) 2.183(6) Å] are typical for \( \sigma \)-bonding distances. Examination of the C-N bond lengths within the CN\(_3\) core of the guanidinate [C(1)-N(1) 1.364(10) Å, C(1)-N(2) 1.306(9) Å, C(1)-N(3) 1.431(9) Å] indicates some delocalisation across the N(1)-C(1)-N(2) skeleton. However, with the much longer distance to the nonligating nitrogen a more localised picture of bonding would appear appropriate.

The reactions of the amidoaluminium complexes \( \text{AlX}_2Y \) (\( X = \text{Cl}, \text{R}; Y = \text{NR}^\text{t}_2 \)) with 1,3-diisopropyl- and 1,3-di-\textit{tert}-butylcarbodiimides were also reported by this group.\(^{(1,44)}\) Pyrolysis of 1,3-diisopropylcarbodiimide with (diisopropylamido)aluminium chloride at 150°C in a sealed tube under vacuum yielded colourless crystals of the compound \( [\text{Cl}_2\text{Al}\{\text{PrN}(\text{NPri}_2)\text{NPri}\}] \), the structure of which was determined by X-ray crystallography (Fig. 1.30). The structure confirms the migration of the diisopropylamido ligand to the central carbodiimide.
carbon, producing the monoanionic tetraisopropylguanidinate ligand. In the complex the distorted tetrahedral coordination geometry of the aluminium comprises the bidentate guanidinate ligand and two chlorides. The guanidinate ligand is symmetrically bound to the metal centre [Al-N(1) and Al-N(2) 1.868(4) Å] as are the two chlorides [Al-Cl(1) 2.113(2) Å and Al-Cl(2) 2.117(2) Å]. In this complex the three C-N bond lengths in the guanidinate moiety are similar [C(1)-N(1) and C(1)-N(2) 1.355(5) Å, C(1)-N(3) 1.366(5) Å] and are shorter than single bonds indicating partial double bond character for these bonds and charge delocalisation within this system. Analogous reactions with diethylamidoaluminium chloride, dialkylamidoaluminium and 1,3-di-tert-butylcarbodiimide were also reported and these were all characterised spectroscopically.

A very recent paper again describes the formation of aluminium alkyl guanidinate complexes though these were prepared in different reactions from those previously reviewed.\(^{(145)}\) The reaction of the aluminium complexes [AlX₂Cl, X = Cl, Me] with lithiated guanidines (formed \textit{in situ} by the reaction of 1,3-diisopropylcarbodiimide with lithium amides) resulted in the formation of chelating tetrasubstituted guanidinate ligand complexes. Specifically, reaction of 1,3-diisopropylcarbodiimide with lithium dimethylamide [LiNMe₂] provided the monolithiated diisopropyl-dimethylguanidinate species. A crystalline product of the reaction of this with AlCl₃ was isolated and the X-ray crystal structure determined (Fig. 1.31). This complex [{Me₂NC(NiPr)₂}AlCl₂] which exhibits distorted tetrahedral geometry has the aluminium ligated by two chlorides and a chelating guanidinate, similar to the structures reported by Chang \textit{et al} (see above). The guanidinate is symmetrically bound [Al-N(1) 1.873(4) Å, Al-N(2) 1.870(4) Å] and the four membered Al-N-C-N chelate rings are essentially planar. The C-N bonds of the guanidine moiety are intermediate in length between single

\[\text{Figure 1.30.}\]

\[\text{Figure 1.31.}\]
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and double bonds [C(3)-N(1) 1.356(6) Å, C(3)-N(2) 1.360(5) Å, C(3)-N(3) 1.343(5) Å] indicating that the negative charge is delocalised over the ligand.

All these examples of chelating guanidinate ligands serve to show that they are very good chelators, forming complexes with a variety of metals. They have a range of substituents, both alkyl and aryl, and also differing amounts of substituents, from two to four. The more recent examples, namely those coordinated to magnesium and aluminium are similar in structure to amidinate complexes that have shown promise as olefin polymerisation catalysts though there was no report of catalytic trials in the papers.

1.5.2 BRIDGING GUANIDINATE LIGANDS

There is a wide diversity in the bridging modes that guanidinates have been shown to adopt and also to the range of metals which they bridge. Complexes are known in which the guanidinate bridges through one, two or all three central nitrogen atoms. Complexes are known for the alkali metals, through the range of transition metals and also for main group metals. These complexes are reviewed in this section.

1.5.2.1 BRIDGING THROUGH ONE NITROGEN

The first report of a monoanionic guanidinate complex was published by Wade et al in 1968.\(^{146}\) Reaction of tetramethylguanidine with MeLi in ether at -40°C smoothly evolved methane and provided the complex \[\{(\text{Me}_2\text{N})_2\text{C}=\text{NLi}\}\], which existed as a dimer in benzene (by cryoscopy). The \(^1\)H NMR spectrum of this is very similar to that of the free ligand confirming that the guanidine is bound via the imine nitrogen alone. This is very similar to the aluminium compounds discussed in the earlier section (page 8) on neutral guanidines.

As part of their study of the reaction of cyclopentadienyl complexes of heavy p block metals with nucleophiles Wright et al examined the 1:1 molar reaction of \(\text{Cp}_2\text{Sn}\) with lithiated tetramethylguanidine \[\{\text{LiN}=\text{C(\text{NMMe}_2)}_2\}\].\(^{147}\) The product of the reaction was found to be that of nucleophilic substitution of one \(\text{Cp}\) ligand to
form the dimeric complex $[(\eta^1\text-Cp)\text{Sn}\{\mu_2-N=C\text(NMe}_2\text{)\}_2]$ (Fig. 1.32). The X-ray crystal structure of the product showed the dimer to be centrosymmetric with a planar Sn$_2$N$_2$ ring. The imino groups bridge the Sn centres almost symmetrically [Sn(1)-N(1) 2.196(3) Å and Sn(1)-N(1a) 2.185(3) Å] and there is considerable distortion within the ring [N-Sn-N 75.36(12)$^\circ$ and Sn-N-Sn 104.64(12)$^\circ$]. Comparison of the C-N bond lengths within the central CN$_3$ ring of the guanidine moiety shows there to be no delocalisation of electronic charge, with the imino bond retaining its double bond character [C(6)-N(1) 1.294(5) Å, C(6)-N(2) and C(6)-N(3) 1.371(5) Å]. In the solid state the complex adopts a trans configuration though $^1$H NMR studies in THF showed the presence of a cis isomer (1:1 at +25°C) also.

1.5.2.2 BRIDGING THROUGH TWO NITROGENS

Thermolysis of guanidine and methylguanidine with Ru$_3$(CO)$_{12}$ in THF produced interesting complexes in which the guanidine is bound to all three Ru atoms on one face of the cluster (Fig. 1.33). The mechanism of the reaction is thought to proceed via a hydrogen atom transfer to form a $\mu_2$-hydride on the Ru$_3$ skeleton. The monoanionic guanidine then binds to the cluster with the Ru$_2$ bridged by the $\mu_2$-hydride also bridged by the guanidine and the third Ru atom coordinated by a monodentate nitrogen.

The reaction of [Pt(trpy)Cl]Cl with guanidinium carbonate in aqueous solution yielded [{Pt(trpy)}$_2$ (guan)], which has a similar structure to the dimer discussed in the earlier section on neutral guanidines (Fig. 1.34). In contrast to the first example however, the guanidine in this complex is truly monoanionic with the negative charge present on the guanidine framework. This does not have a dramatic effect on the geometry of the complex in the solid state which is closely related to the example where the guanidine is neutral. The Pt-Pt separation is 3.071(1) Å and the
trpy ligands are nearly parallel to each other [angle between planes 9°]. They adopt a slightly staggered conformation in the solid state although they show only one set of peaks in the $^{13}$C NMR spectrum indicating they are equivalent in solution. The guanidinate is symmetrically coordinated to the metals [Pt(1)-N(7) and Pt(2)-N(8) both 2.00(1) Å] which is slightly more tightly bound than for the neutral example, as would be expected for this anionic ligand.

Recently, there has been a number of reports describing the formation of tetrabridged dimers which adopt the paddlewheel (or lantern) structure [M$_2$L$_4$X$_2$] (where L = bridging ligand, X = axial ligand). The first complex of this type containing a trisubstituted guanidinate was formed in the reaction of 1,2,3-triphenylguanidine with Mo(CO)$_6$ under reflux in diglyme solution. The isolated product [Mo$_2${μ-η$^2$-(PhN)$_2$CNHPh}$_4$] was structurally characterised as the quadruply bonded Mo$_2$ dimer with a Mo-Mo separation of 2.0839(9) Å (Fig. 1.35). The dimer is bridged by four guanidinate ligands in a paddlewheel arrangement with two ligands crystallographically independent. The four Mo-N distances do not vary significantly [range 2.156(5) to 2.179(4) Å] and the CN$_3$ units of the guanidines are essentially planar. Hydrogen atoms were located on the noncoordinating nitrogens in Fourier difference maps, confirming the monoanionic character of the ligands.

The yellow product was found to be very air sensitive and cyclic voltammetry in CH$_2$Cl$_2$ solution showed two reversible one-electron oxidation waves at -0.05 and +0.85 V vs Ag/AgCl waves corresponding to the [Mo$_2$]$^{4+/5+}$ and [Mo$_2$]$^{5+/6+}$ couples. The deep red monocation [Mo$_2${μ-η$^2$-(PhN)$_2$CNHPh}$_4$]$^+$ and the dark blue dication [Mo$_2${μ-η$^2$-(PhN)$_2$CNHPh}$_4$]$^{2+}$ could also be prepared by chemical oxidation.
using silver tetrafluoroborate or ammonium cerium(IV) nitrate respectively. The crystal structure of the monocationic species was obtained as the tetrafluoroborate salt, \([\text{Mo}_2\{\mu-\eta^2-(\text{PhN})_2\text{CNHPh}\}_4][\text{BF}_4]\), although attempts to crystallise the dication failed due to reduction of the species to the monocation during crystallisation. The monocation has a similar structure to the neutral species with a Mo-Mo separation of 2.1194(12) Å.\(^1\) As with the neutral species, there is no axial ligation of the Mo centres as substituent phenyl groups block these sites [shortest Mo-F (BF\(_4\)) 6.035 Å]. The fact that the neutral complex is readily oxidised indicates that the guanidinate ligand is effective at stabilising the oxidised species, i.e. the ligands are able to donate more electron density to the metal centres. This was rationalised by involvement of a resonance form of the ligand in which the uncoordinated nitrogen lone pair is delocalised into the ligand \(\pi\)-system thus increasing the \(\pi\)-basicity of the coordinated nitrogen atoms (Fig. 1.36). Indeed, there is some evidence from the crystal structure of the monocation that there is a greater contribution from resonance form B than is observed for the neutral complex.

**METAL DIMERS BRIDGED BY THE HPF ION**

1,3,4,6,7,8-hexahydro-2H-pyrimidino[1,2-\(\alpha\)]pyrimidine (Hpfp) (Fig. 1.37a) is a hetero-bicyclic compound which contains a guanidine moiety. In relation to the other guanidines described it can be considered as a tetrasubstituted guanidine, though its bicyclic nature increases the rigidity of the molecule. A feature of this rigidity is that the lone pairs on the nitrogens are parallel to each other, an ideal situation for bridging two metals.

The first Hpfp bridged dimer was a paramagnetic diruthenium(III) complex described by Bear et al.\(^{1,51}\) The X-ray crystal structure was determined and the complex found to be [Ru\(_2\)hpfp\(_4\)Cl\(_2\)] (Fig.1.37b). The geometry around the ruthenium centres is essentially octahedral with four hpfp nitrogens in the equatorial sites [Ru-
N(1) 2.045(5) Å, Ru-N(1') 2.063(5) Å and a chloride in an axial position [Ru-Cl 2.705(2) Å]. The Ru-Ru bond distance of 2.321(1) Å was not considered unusual with regard to the theoretical bond order of 3 for Ru₄⁶⁺ systems. The three C-N bond lengths within the guanidine moiety are similar [C(1)-N(1) 1.332(6) Å, C(1)-N(1') 1.352(5) Å, C(1)-N(2) 1.363(7) Å] and intermediate between single and double bonds indicating some delocalisation over these bonds. The cyclic voltammogram of the complex showed two reversible one-electron processes: reduction at $E_{1/2} = -0.60$ V and oxidation at $E_{1/2} = 0.55$ V. The magnetic susceptibility of the complex 2.78 $\mu_B$ is consistent with a system containing two unpaired electrons. From these data the ground state electronic configuration was determined to be either $(\sigma^2)(\pi^4)(\delta^2)(\pi^*)^2$ or $(\sigma^2)(\pi^4)(\delta^2)(\pi^*)(\delta^*)^1$.

Cotton et al have recently published a series of papers in which they describe the formation and structure of various hpp-bridged metal dimers. Their interest in this bicyclic ligand resulted from the desire to synthesise dimeric compounds containing ligands with similar properties to amidinates, though with greater resistance to cleavage. The first of these publications detailed the synthesis of V₂⁴⁺, Cr₂⁴⁺ and Mo₂⁴⁺ compounds which are all tetrabridged by the monoanionic hpp ligand. Reduction of VCl₃(THF)₃ at -78°C, followed by addition of two molar equivalents of Li[hpp] produced a toluene soluble brown powder from which crystals were obtained. X-ray structural analysis of this complex confirmed that the complex adopts a paddlewheel structure with a very short V-V bond [1.932(1) Å] (Fig. 1.38). The molecule lies on an inversion centre and the five-membered chelate rings [M-M-N-C-N] are essentially planar The hpp is symmetrically coordinated to the metal centres [e.g. V(1)-N(11) 2.061(4) Å] and within the guanidinium framework the C-N distances are consistent with partial bond character [av. C(17)-N 1.35(2) Å].
Synthesis of the dimolybdenum complex was achieved by the reaction of Mo$_2$(O$_2$CCF$_3$)$_4$ with Li[hpp] in toluene solution. Crystals obtained from this solution were found to be crystallographically similar to the divanadium complex. The Mo-Mo distance of 2.067(1) Å is very short in comparison to other molybdenum paddlewheels with nitrogen donor atom bridges while the coordinate bonds are crystallographically equivalent [Mo(1)-N(11) 2.159(6) Å, Mo(1)-N(12)' 2.167(6) Å].

Reaction of Li[hpp] with anhydrous CrCl$_2$ at -78°C provided a yellow solution from which a highly air and water sensitive product was obtained. X-ray structural analysis of the product confirmed that it was Cr$_2$(hpp)$_4$, though the crystal packing differed slightly from the previous examples. Again, the molecule has an inversion centre and the coordinate bonds are crystallographically equivalent [e.g. Cr(1)-N(11) 2.041(2) Å]. The central CN$_3$ core of the guanidinate ligands are again planar with C-N bonds averaging 1.35(2) Å and the Cr-Cr distance [1.8517(7) Å] is short in comparison to other nitrogen bridged systems.

A communication discussing the bond lengths in dimolybdenum complexes was also published by this group. The synthesis of [Mo$_2$(hpp)$_4$(BF$_4$)$_2$] by the oxidation of Mo$_2$(hpp)$_4$ was described and its X-ray crystal structure presented (Fig. 1.39). The paddlewheel structure of the starting material is maintained, the only major difference being the weak coordination of the BF$_4^-$ anions in axial sites [Mo(1)···F(3) 2.768(6) Å]. The central Mo$_2$ unit has a formal triple bond with a Mo-Mo distance of 2.142(2) Å, an increase of 0.075 Å from the quadruply bonded Mo$_2^{4+}$ described previously. The Mo-N distances are shorter than observed for the neutral system [av. 2.08(7) Å]. The communication highlights the error in Mo-Mo bond length given for the monocationic [Mo$_2${μ-η$:1^\prime}$^-$\(\text{PhN})_2\text{CNHPh}_{4}^+$ system (page 25) though this had previously been corrected (see ref. 1-50b).

A further publication by this group detailed the synthesis of a dimeric, triply bonded niobium complex [Nb$_2$(hpp)$_4$] in which the Nb-Nb distance 2.2035(9) Å, is
the shortest known.\textsuperscript{(1-54)} The complex was formed by the reaction of NbCl\textsubscript{5}(DME) and Li[hpp] in the presence of KC\textsubscript{8} at room temperature in THF and produced green crystals of the diamagnetic product. An X-ray crystal study confirmed the complex to exist in a paddlewheel arrangement, similar to the vanadium, chromium and molybdenum complexes previously described, with the Nb\textsuperscript{2+} unit bridged by four monoanionic hpp ligands (Fig. 1.40). The dimer is centrosymmetric with crystallographically symmetrical coordinate bonds [Nb(1)-N(11) 2.201(4) Å, Nb(1a)-N(12) 2.198(4) Å]. The guanidinate ligand has a planar CN\textsubscript{3} core [angles at C(17) total 360\textdegree], while the coordinated nitrogens have shorter bonds to the central carbon [C(17)-N(11) 1.347(7) Å, C(17)-N(12) 1.332(7) Å] indicating partial double bond character of these bonds. Of added interest is the Nb-Nb triple bond in this complex is very short, indeed it is considerably shorter than the Nb-Nb distance in the metal itself (2.85 Å).

A final paper from this research group outlined the formation of a copper(I) dimer containing a very short nonbonded contact.\textsuperscript{(1-56)} The reaction of CuCl with Li[hpp] in THF at -78\textdegree C yielded a white precipitate from which colourless crystal were readily obtained. X-ray structural analysis of these revealed that the Cu(I) centres are bridged by two monoanionic hpp ligands (Fig. 1.41). The ligands are symmetrically coordinated [Cu(1)-N(11) 1.862 Å, Cu(1)-N(12a) 1.863 Å] while the Cu-Cu separation of 2.4527(10) Å is somewhat shorter than previously observed for complexes of this type. For the guanidinate ligands themselves, the central CN\textsubscript{3} unit is planar while there is some variation of the bonds within this unit [C(17)-N(11) 1.339(5) Å, C(17)-N(12) 1.346(5) Å, C(17)-N(13) 1.371(5) Å] indicating partial double bond character within the guanidine moiety. DFT calculations were used on this system in order to confirm that there is no bonding
interaction between the two copper centres. The close contact between the two metals was thought to be due to a combination of strong Cu-N bonding and very short bite distances for the ligands.

The reaction of AlMe₃ with Hhpp was reported in the same article as described the reaction of alkylaluminium complexes with lithiated guanidines. Methane was evolved during the reaction and the product was crystallised from THF. An X-ray crystal structure determination confirmed the product to be [(μ-hpp)AlMe₂]₂, a dimer in which the hpp ligands link the two AlMe₂ units forming an eight-membered ring with a chair conformation (Fig. 1.42). The geometry at the aluminium centres is tetrahedral with average Al-N distance of 1.918 Å. The CN₃ core of the hpp ligand is planar with intermediate C-N distances [C(7)-N(1) 1.348(3) Å, C(7)-N(2) 1.346(3) Å, C(7)-N(3) 1.357(3) Å] again indicative of charge delocalisation though comparison with the previous example is complicated by the bicyclic nature of this ligand.

1.5.2.3 BRIDGING THROUGH THREE NITROGENS

The X-ray crystal structure of the product obtained from the reaction between tetramethylguanidine and BuLi in ether was reported. The crystalline product isolated from this reaction was found to exist as a hexamer [Li{N=C(NMe₂)₂}]₆ (Fig. 1.43). The Li₆ rings form a chair-shaped structure with the lithium atoms held together by triply bridging N=C(NMe₂)₂ groups. These bridging nitrogens are approximately equidistant from the three Li atoms it binds to [Li-N distances 1.98, 2.00 and 2.02 Å]. Within the hexameric unit, 24 valence electrons are available for the 18 Li-N contacts resulting in a formal Li-N bond order
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of 0.66. Therefore locally, each ligand nitrogen has two electron pairs to bond to three Li atoms so one two-centre bond and one three-centre bond must exist. As the nitrogen is symmetrically bound to the lithiums these bonding systems must be delocalised.

Chivers et al recently reported the crystal structures of mono- and dilithiated tri-tert-butylguanidine.\(^{(1-57)}\) The monolithiate was synthesised in the low temperature reaction between 1,3-di-tert-butylcarbodiimide and lithium tert-butylamine and crystallised from THF. The X-ray crystal structure was determined and was found to have the composition \([\text{Li}\{\text{C(NtBu)}_2(\text{HNtBu})\}]_2(\text{THF})\) which forms an eight-membered \(\text{Li}_2\text{N}_4\text{C}_2\) ring in the solid state (Fig. 1.44). The two guanidinate monoanions are bridged by the lithium atoms, one of which is solvated by THF. The C-N bond distances of 1.32(1) Å and 1.37(1) Å within the ring suggest a tendency towards single and double bonds and only limited delocalisation of negative charge. The exocyclic C-N bonds [1.39(1) Å] are consistent with a single bond and the presence of a hydrogen on these nitrogens. The CN₃ moieties are planar with the sum of angles around the central carbon totalling 360°.

Deprotonation of the monoanion with \(n\)-BuLi yielded the dilithiated complex which was crystallised from pentane to give the unsolvated \([\text{Li}_2\{\text{C(NBu)}_3\}]_2\). In the X-ray crystal structure this was found to exist as \(\text{C}_2\text{N}_6\text{Li}_4\) cages which incorporate two planar guanidinate dianions linked by four three coordinate lithium atoms (Fig. 1.45). Within the CN₃ core of the guanidinates the C-N bond distances average 1.379(7) Å which is consistent with single bonds. The overall structure of the cage can be viewed as a distorted cyclic ladder or alternatively as a highly distorted hexagonal prism. This is in marked contrast to the structure of the
dilithiated tri-phenylguanidine which will be described in the later section on dianionic guanidines.

The articles discussed show that monoanionic guanidinates are highly versatile bridging ligands and are capable of bridging a multitude of metals including alkali, transition and main group in a variety of different modes.

1.6 Complexes Containing Dianionic Guanidines

There are considerably fewer examples of complexes containing a dianionic guanidine ligand than for the previously discussed monoanionic or neutral ligands. Indeed, to date, there are only five reports of ligands of this type and in these the guanidines are found to exhibit a variety of coordination geometries. Of further note is that all the guanidines described in this section are trisubstituted.

The first example, published by Farona et al., describes the product of the mechanistically obscure reaction between Fe(CO)$_5$ and dialkylcarbodiimides in refluxing heptane. Spectroscopic analysis of the resultant orange crystalline product pointed to the product containing a dianionic guanidinate bound across a Fe$_2$(CO)$_6$ unit (Fig. 1.46). This was reported to have been confirmed by an X-ray diffraction study although the data and resulting structure have apparently never been published.

The first crystallographically characterised dianionic guanidine complex, the THF solvated dimer [Li$_2${C(NPh)$_3$}]$_2$ (Fig. 1.47), was reported by Bailey et al. In this structure the trisubstituted guanidine units are bridged by two lithium atoms, each coordinated by three nitrogens and a THF molecule. The two remaining lithium atoms are coordinated to the third nitrogen on each guanidine, an ipsoC-orthoC C-C bond of an adjacent phenyl ring and two THF molecules. Within the CN$_3$ central core the C-N bond lengths show no
significant difference (average 1.36 Å) so there is no evidence for a localised double bond. Also, the sum of angles around the central C totals 360°, indicating a strict planarity of the CN₃ core and therefore significant π delocalisation (Y-conjugation) around this carbon. In agreement with this is the sp² hybridisation of the nitrogens (mean C-N-C 121.6°) as would be required for such an electronic distribution.

An interesting product was obtained in the reaction between dilithio-triphenylguanidine [((PhN)₃C)Li₂] and cadmium bis(trimethylsilylamide) [Cd{N(SiMe₃)₂}₂], as described by Bailey et al. The expected product of this reaction would be that of nucleophilic substitution of {N(SiMe₃)₂} by {PhN)₃C}. This however, does not occur and the isolated product was the co-complex of the two reaction components [((Me₃Si)₂N)Cd{(PhN)₃C}Li₂·3thf] (Fig. 1.48). The guanidine unit is bound to the Cd via one nitrogen only [Cd(1)-N(11) 2.213(4) Å] and this nitrogen is also bound to one lithium. The other two nitrogen atoms of the guanidine are coordinated to two independent THF solvated lithium atoms.

A number of similarities between this structure and that obtained for the dilithio-triphenylguanidine were observed. The average C-N bond length in the CN₃ core is again 1.36 Å although as a result of coordination to the Cd the C(10)-N(11) bond is slightly lengthened in comparison with the C(10)-N(12) and C(10)-N(13) bonds [1.376(7) Å vs. 1.350(7) Å and 1.358(7) Å respectively]. The sum of angles around the central carbon of the CN₃ core again totals 360° indicating some delocalisation in the guanidine moiety. The fact that the adduct is stable to [Li{N(SiMe₃)₂}] elimination may also give an indication of the extensive resonance stabilisation exhibited by the guanidine ligand upon the adduct as a whole. A final similarity between the two structures is in the arrangement of the substituent phenyl groups which again adopt a trans, trans, cis conformation about the central carbon. This can be rationalised by the fact that in this arrangement the nitrogen lone pairs can point towards the Li⁺ cations.
The reaction of N,N',N''-triphenylguanidine with [PtCl₂(cod)] in dichloromethane, mediated by silver (I) oxide, yielded the first mononuclear dianionic guanidine complex [Pt{NPhC(NPh)NPh}(cod)]. An X-ray crystal structure determination of this complex confirmed that the guanidine was bound η² to the Pt centre, forming a planar, four-membered Pt-N-C-N metallacycle (Fig. 1.49). In contrast to the previous example the C-N bond lengths in the guanidine unit differ considerably [C(1)-N(1) and C(1)-N(2) are 1.40(1) Å; C(1)-N(3) is 1.30(1) Å] indicating localised double and single bonds. In agreement with the dilithio dimer though is the planarity of the central CN₃ unit, with the angles around the central carbon again totalling 360°. The Pt-N coordinate bonds show a slight difference [Pt-N(1) is 2.034(8) Å and Pt-N(2) is 2.002(7) Å], though this is thought to be as a result of steric interactions between phenyl substituents on N(1) and N(3) and not indicative of a difference in donor ability of the nitrogens.

A report of transition metal complexes containing dianionic guanidinate ions as ligands was recently published by Henderson et al. The paper describes the synthesis of Ru(II), Os(II), Rh(III), Ir(III) and Pt(II) complexes containing chelating guanidinate ligands, formed in the reaction of trisubstituted guanidines (phenyl or acetyl) with metal halides mediated by silver(I) oxide. This procedure was first utilised in the previous communication in which the structure of [(COD)Pt{NPhC(=NPh)NPh}] was described. The synthesis and characterisation of this complex and of the novel complexes [Cp*M{NAcC(=NAc)NAc} (PPh₃)] (M = Rh, Ir) and [(p-cymene)M{NAcC(=NAc)NAc} (PPh₃)] (M = Ru, Os) were provided in detail. The
X-ray crystal structure of [(p-cymene)Ru(\text{NAC}(=\text{NAC})\text{NAC})(\text{PPh}_3)] (Fig. 1.50) was described although due to problems in structure refinement, no discussion of its metrical parameters were given, the structure serving only to confirm that the guanidinate ligand does indeed act as a chelating ligand to the ruthenium centre. Therefore, characterisation of the complexes was achieved by the unambiguous assignment of a series of NMR experiments including NOE, $^1\text{H}-^1\text{C}$ COSY and long range BIRDTRAP ($^1J$ suppression) $^1\text{H}-^1\text{C}$ COSY. Electrospray mass spectrometry was also employed very successfully in this study, very strong peaks from parent ions being observed. Interestingly, when the complexes which contained a triphenylphosphine ligand were analysed using acetonitrile solutions, ions of the type [M - PPh$_3$ + MeCN]$^+$ were commonly found, the lability of the phosphine ligand being a direct result of steric crowding at the metal centre.

To summarise, although as yet there are only a few examples of dianionic guanidine ligands, a diversity already exists in the range of metals with which they interact (alkali, transition, main group) and also in the mode in which these ligands coordinate. There is also evidence for their being two distinct electronic distributions which the ligand can adopt, either localised or delocalised, which seems dependant on whether the lone pair on the third nitrogen is involved in coordination to a metal centre.

1.7 SUMMARY OF CURRENT LITERATURE

This review of literature serves to emphasise the wealth of metallo-organic complexes which contain either neutral or anionic guanidine ligands. There is a vast array of coordination modes which are available to guanidine ligands, which is in no way diminished by the ready accessibility of their deprotonated forms. While having no dramatic effect on ligand properties, it would be expected that variation of substituent groups on the ligand would alter the characteristics of the complexes. It is unfortunate that no direct comparison of this has been made in the literature to date.

However, although many papers relating to guanidine ligands are known, at the outset of this work reports of guanidine ligands were uncommon and those
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pertaining to trisubstituted guanidines were very scarce indeed. Given the similarity of guanidines to amidines and triazines this oversight was quite surprising and it is maybe for this reason that the area of guanidine ligand chemistry has blossomed. This increase in interest can be gauged by the sheer volume of work relating to complexes containing guanidine ligands which has been published in the last few years.

The following chapters in this thesis will describe the work which I have undertaken with guanidine ligands and hope to prove that they are versatile ligands for metallo-organic chemistry.
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1.4 REFERENCES


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SYNTHESIS OF SUBSTITUTED GUANIDINES

In order to be able to synthesize guanidinate metal complexes suitable for asymmetric catalysis, it was necessary to synthesize guanidines containing either chiral or sterically demanding groups (in order to force C₃ symmetry in the complexes). This chapter describes in detail, the synthesis of substituted guanidines containing a variety of alkyl and aryl groups. Development of a synthetic route which allows permutation of these groups gives access to a range of ligands which can have their steric and electronic properties varied systematically. The compounds synthesised are mainly tri-substituted though synthesis of a tetra-substituted guanidine is also described. The synthesis and full characterization of a guanidine containing homochiral substituents is also presented herein. Some of this work was undertaken by people in the research group and acknowledgment of this is made where appropriate.

2.1 SYNTHESIS OF TRI-SUBSTITUTED GUANIDINE DERIVATIVES

The preliminary work carried out in the project was to synthesise and characterise tri-substituted guanidines, in particular N,N',N''-tri-(p-tolyl)guanidine. This particular derivative would be attractive as a ligand as the p-methyl moieties would act as useful NMR reporting groups to aid the determination of the mode of the coordination of the ligand to the metal while maintaining aromatic substituents which were known to promote crystallisation.

There are numerous methods reported in the literature for the synthesis of guanidines, as reviewed by Yamamoto and Kojima, the most straightforward being the addition of a primary amine to a carbodiimide (Fig. 2.1).

\[
R\text{-}N\equiv C\equiv N\text{-}R' \quad + \quad R''NH_2 \quad \rightarrow \quad R\text{HN}N\equiv NHR''
\]

*Figure 2.1. General route to trisubstituted guanidines.*
The first guanidine prepared by this method was the triphenyl derivative, by reacting diphenylcarbodiimide (itself synthesised by cracking phenylisocyanate with iron pentacarbonyl\(^{2-3}\)) with aniline in refluxing toluene, producing the guanidine 21 (Fig. 2.2) in a 84\% yield.\(^{2-2}\) This was fully characterised spectroscopically although the assignment of peaks in the aromatic region of the \(^{13}\)C NMR spectrum was uncertain due to the broadening of the peaks by internal exchange within the molecule.

Other trisubstituted guanidines synthesised by this procedure include the triisopropyl (96\% yield) and tricyclohexyl (68\%) derivatives (work carried out by Dr. Keith J. Grant). Their respective carbodiimides required for these reactions were commercially available and their synthesis was therefore unnecessary.

Unfortunately, di-(p-tolyl)carbodiimide is not commercially available and it is not economically viable to synthesise di(p-tolyl)carbodiimide from p-tolyl isocyanate so an alternative method was required to produce the p-tolyl derivative.

2.1.1 SYNTHESIS OF \(N,N',N'\)-TRI-(P-TOLYL)GUANIDINE

It was found that carbodiimdes could be readily prepared from thioureas\(^{2-2}\) (Fig. 2.3) which were readily synthesisable themselves so this route seemed a good point of entry to di-(p-tolyl)carbodiimide and was the first method to be attempted.

\[
\begin{align*}
R\text{NH}_2 & \rightarrow R\text{HN} & \rightarrow R-N=N-C=N-R \\
\text{R} & = \text{p-tolyl} \\
\end{align*}
\]

\(\text{Figure 2.3. Synthesis of carbodiimde via thiourea.}\)

\(N,N'\)-di-(p-tolyl)thiourea 22 was prepared as reported by N. Yamazaki, et al,\(^{2-4}\) from p-toluidine and carbon disulphide, in the presence of imidazole and diphenyl phosphite. The product was isolated as a yellow powder, in a yield of 64\% and was fully characterised.
2.1.1.1 ATTEMPTED SYNTHESIS OF DI-(p-TOLYL)CARBODIIMIDE

The method reported by White and Mullin\(^1\) was used for the first attempt at the synthesis of the carbodiimide. This involved refluxing the thiourea in water in the presence of lead(II) oxide which formally results in the loss of H\(_2\)S from the thiourea. However the reaction is known to go via urea as an intermediate with the lead being converted into lead(II) sulphide in the process. Isolation of the product produced a sticky oil which showed no characteristic band in the IR spectrum\(^2\) due to carbodiimide. N\(_2\)N’-di-(p-tolyl)urea was isolated as a by-product and identified by its strong band in the IR spectrum at 1640 cm\(^{-1}\).\(^3\) The reported synthesis was for bis-(di-o-tolyl)carbodiimide and this method was also known to work for the di-isopropyl and di-t-butyl derivatives. These three carbodiimides are all very hydrophobic so they will be more resistant to hydrolysis than the di-p-tolyl derivative which is also less sterically hindered around the diimide linkage. Hence, if the carbodiimide does form in the reaction then it is likely that it would hydrolyse and reform the urea.

2.1.1.1b ATTEMPTED SYNTHESIS OF DI-(p-TOLYL)CARBODIIMIDE

An alternative method for the synthesis was that reported by Ruby.\(^4\) It made use of a biphasic system of toluene and water which was hoped to diminish the hydrolysis of the carbodiimide. Lead(II) oxide was again used as the reagent and elemental sulphur and sodium chloride were also added to the reaction mixture. The synthesis was successful although the carbodiimide was only produced in a relatively poor yield (46\%). It also proved difficult to purify the product due to contamination by the urea by-product.

2.1.1.1c ATTEMPTED SYNTHESIS OF DI-(p-TOLYL)CARBODIIMIDE

At this stage it was realised that the main problem with the synthesis of the di-(p-tolyl)carbodiimide was the hydrolysis of the product back to the urea. Hence, an alternative method that did not involve the use of water as a solvent was required.
Zetzsche and Nergert\(^{(2-8)}\) reported a synthesis of di-(p-tolyl)carbodiimide that was performed in acetone. Lead(II) oxide was again used as the reagent with elemental sulphur and under reflux the reaction was reported to go to completion within a few hours. However, it was determined by IR that some of the carbodiimide had formed but the majority of the product was again the urea derivative. The experiment was repeated in the strict absence of water but even after 48 hours of refluxing no carbodiimide had formed.

2.1.1.2 SYNTHESIS OF N,N',N''-TRI-(p-TOLYL)GUANIDINIUM SALT

The synthesis of the desired carbodiimide was proving problematic so an alternative route to guanidine derivatives was sought. Smidt and Andrieth\(^{(2-9)}\) reported the conversion of a substituted thiourea to its Mel salt (Fig. 2.4, 1st step). The N,N'-di-(p-tolyl)thiourea was treated with methyl iodide in dimethoxyether to form S-methyl-di-(p-tolyl)isothiuronium iodide 23 in almost quantitative yield.

\[
\text{RHN} \quad \overset{\text{MeI}}{\longrightarrow} \quad \text{S} \quad \overset{\text{Me}}{\longrightarrow} \quad \text{NHR} \\
\text{NHR} \quad \overset{\text{RHN}}{\longrightarrow} \quad \text{S} \quad \overset{\text{NHR}}{\longrightarrow} \quad \text{Me} \\
\]

*Figure 2.4. Synthesis of guanidinium iodide via isothiuronium salt.*

It was anticipated that reaction of this salt with p-toluidine would yield N,N',N''-tri-(p-tolyl)guanidinium iodide\(^{(2-10,2-11)}\) (Fig. 2.4, 2nd step) from which isolation of the free guanidine should be possible.\(^{(2-12)}\) The reaction of p-toluidine with the isothiuronium salt was attempted in DME and after the prominent S-CH\(_3\) singlet had disappeared from the \(^1\)H NMR spectrum of the reaction mixture, isolation and purification of the product yielded a pale yellow solid. However, in the \(^1\)H NMR spectrum, the integral of the NH peak was much larger than expected relative to the other peaks and in the \(^{13}\)C NMR spectrum there was no peak due to the central quaternary C (expected at \(\delta\) 140-150 ppm). The nominal mass spectrum only showed
one prominent peak at \( m/z \) 108 from which it was concluded that the isolated product was in fact the HI salt of \( p \)-toluidine (Fig. 2.4).

A second attempt at this synthesis in ethanol was also unsuccessful, unreacted starting material being all that was isolated from the reaction mixture.

As this route to \( N,N',N'' \)-tri-(\( p \)-tolyl)guanidine was also proving problematic it was decided to attempt the synthesis of the carbodiimide from the thiourea once again. After an extensive search of the literature, a new method for the synthesis was found which was attempted.

### 2.1.1.1D SYNTHESIS OF DI-(\( p \)-TOLYL)CARBODIIMIDE

The synthesis of di-(\( p \)-tolyl)carbodiimide was finally achieved using the method of Appel, et al.\(^{(2-13)}\) in which a thiourea is converted to a carbodiimide in the presence of triphenylphosphate, carbon tetrachloride and triethylamine (Fig. 2.5). The mechanistically obscure reaction was reported to proceed via an intermediate and produces carbodiimide with triphenylphosphine sulphide as one of the by-products.

\[
\text{S}
\begin{array}{c}
RHN
\end{array}
\text{NHR}
\xrightarrow{\text{Ph}_3\text{P} + \text{CCl}_4 + \text{Et}_3\text{N}}
\begin{array}{c}
R
\end{array}
\begin{array}{c}
\text{N}
\end{array}
\begin{array}{c}
\text{C}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
\begin{array}{c}
R
\end{array}
\text{Ph}_3\text{P=}=\text{S} + \text{HCCl}_3 + \text{Et}_3\text{NHCl}
\]

*Figure 2.5. Alternative synthesis of di-(\( p \)-tolyl)carbodiimide.*

The product was isolated by distillation although it proved very difficult to remove all traces of the triphenylphosphine sulphide impurity. The final yield (30%) of the yellow oil was rather poor though it was the best synthetic route that had been found for di-(\( p \)-tolyl)carbodiimide 24.

After the carbodiimide had been synthesised it was straightforward to use this to produce \( N,N',N'' \)-tri-(\( p \)-tolyl)guanidine 25 by reacting the carbodiimide with \( p \)-toluidine in refluxing toluene as outlined previously.\(^{(2-2)}\) Recrystallisation of the product was attempted in many solvents though di-isopropyl ether was found to yield the most crystalline product (76% yield). The compound was fully characterised
spectroscopically and, similar to the triphenylguanidine, the $^{13}$C NMR had broad peaks in the aromatic region due to the fluxionality of the molecule.22

### 2.1.2 Synthesis of $N,N',N''$-tri-(tert-butyl)guanidine

The synthesis of tri-tert-butylguanidine was undertaken by Dr. Keith J. Grant. Following the methodology used for the other trisubstituted guanidines, reaction of di-(tert-butyl)carbodiimide with tert-butylamine was attempted though only starting materials were recovered. This was thought to be due to increased steric hindrance which prevented the reactants coming close enough to react.

In order to overcome the steric barrier, it was necessary to increase the nucleophilicity of tert-butylamine by lithiating it (Fig. 2.6), a method later reported by Chivers et al.(2-14)

![Figure 2.6. Reaction of carbodiimide with lithiated amine.](image)

Addition of a THF solution of lithio-tert-butylamine to di-(tert-butyl)carbodiimide, yielded a colourless solution with some white precipitate. Warming to room temperature caused dissolution of some of the precipitate though inspection of the solution by infra red spectroscopy revealed that some unreacted carbodiimide remained [$\nu(N=\text{C}=\text{N}) = 2104 \text{ cm}^{-1}$]. Warming of the solution to 50°C for 15 minutes caused the band at 2104 cm$^{-1}$ to recede. The guanidine 26 was obtained by hydrolysis of the reaction mixture and extraction with ether and purified by Kugelrohr distillation.

That $N,N',N''$-tri-(tert-butyl)guanidine is a low boiling liquid and not a solid like the other tri-substituted tri guanidines gives some indication of the steric bulk the tert-butyl groups possess, hindering the packing of the molecules and preventing solidification. Further evidence of the effect that the steric bulk of the tert-butyl groups has on the molecule is observed in its $^1$H and $^{13}$C NMR spectra. In the $^1$H spectrum, the
signal for the methyl groups is very broad and in the $^{13}$C spectrum there are four signals for the methyl carbons and a broad signal for the quaternary carbons. These observations are due to the rotation of the tert-butyl groups being hindered causing these atoms to be in non-equivalent environments on the NMR timescale.

2.1.3 SYNTHESIS OF $N,N',N''$-TRIS((S)-(−)-α—METHYLBENZYL)GUANIDINE

This compound was synthesised by Dr. K.J. Grant following the method used for the other guanidines described.

$N,N',N''$-tris((s)-(−)-α—methylbenzyl)guanidine 27 was synthesised in good yield from bis((s)-(−)-α—methylbenzyl)carbodiimide and ((s)-(−)-α—methylbenzyl)amine in refluxing diglyme. From the reaction mixture an orange oil was obtained which crystallised upon storage at 5°C. The resulting solid was characterised spectroscopically.

With a view to determining the 3D structure of this compound, the hexafluorophosphate salt of this guanidine 28 was synthesised and crystals suitable for X-ray diffraction study were obtained. An X-ray structure determination bore out two interesting points (Fig. 2.7). The molecule has local $C_3$ symmetry with bond lengths and angles identical [C-N 1.327(3) Å, N-C-N 120°]. Furthermore, the CN$_3$ structural unit has steric elements above its plane but none below it, hence it possesses two stereochemically different faces. Using this as a model, facial $γ^3$ coordination of a metal centre would result in a chiral complex with $C_3$ symmetry though due to the homochirality of the substituents on the guanidine only one enantiomer of this complex would form.

<table>
<thead>
<tr>
<th>C-N</th>
<th>1.327(3)</th>
<th>N-C-N(0a)</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-N(0a)</td>
<td>1.327(3)</td>
<td>N-C-N(0b)</td>
<td>120</td>
</tr>
<tr>
<td>C-N(0b)</td>
<td>1.327(3)</td>
<td>N(0a)-C-N(0b)</td>
<td>120</td>
</tr>
</tbody>
</table>

*Table 2.1. Selected bond lengths (Å) and angles (°) for 28.*
Figure 2.7. X-ray crystal structure of \( \text{N,N',N'''-tris((s)-(-)-a-methylbenzyl) guanidinium ion as its hexafluorophosphate salt} \).
2.2 SYNTHESIS OF TETRA-SUBSTITUTED GUANIDINE DERIVATIVES

The syntheses of a tetra-substituted guanidine was undertaken in order to provide molecules which could only be singly deprotonated.

N,N-diethyl-N',N''-diphenylguanidine was first prepared by Uwe Fischbeck, an Erasmus student working under my supervision. Reaction of diphenylcarbodiimide with diethylamine produced the guanidine 29 (Fig. 2.8) in a 62% yield. It was fully characterised spectroscopically and, similar to the N,N',N''-triphenylguanidine, its $^{13}$C NMR spectrum showed broad peaks in the aromatic region caused by internal exchange within the molecule.
2.3 EXPERIMENTAL

Solvents were deoxygenated and dried before use by distillation from sodium / benzophenone for THF and diglyme and CaH₂ for toluene. Acetone was dried by storage over molecular sieves (4Å).

Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FTIR spectrometer. Elemental Analysis was determined using a Perkin Elmer 2400 CHN Elemental Analyser. (+/- FAB) mass spectra were obtained using a Kratos MS50TC spectrometer and +EI spectra on a Finnigan 4500 spectrometer. Nuclear Magnetic Resonance spectra were recorded on Bruker AC200 and Bruker AC250 spectrometers and continuous wave spectra on a Joel PMX-60. Positive chemical shifts were referenced to TMS.

2.3.1 SYNTHESIS OF TRISUBSTITUTED GUANIDINES

2.3.1.1 PREPARATION OF N,N',N' '-TRI(PHENYL)GUANIDINE 21

This was achieved by adapting the method of Mikolajczyk, et al., in which diphenylcarbodiimide (20.01 g, 103 mmol) and aniline (9.59 g, 9.38 cm³, 103 mmol) were dissolved in toluene (200 cm³) and refluxed for 20 hours. Evaporation of the solvent produced a white precipitate which was recrystallised from toluene to yield fluffy, white crystals (24.95 g, 84%); MP = 145°C (lit. 145°C); IR (nujol mull) νmax 3347(w) (N-H), 1635(m) (C=N), 1583(m) & 1554(m) (C-N) cm⁻¹; MS (+ve FAB) : [M+H]+, 288, 195, 133, 91, 77; Accurate mass, Found 288.15100; C₁₉H₁₇N₃ requires 288.15007; Deviation = 3.21 ppm; ¹H NMR (250 MHz, CDCl₃) : δ 5.9 (br,s, 2H, NH), 7.2 (m, 15H, ArH) ppm; ¹³C NMR (62.9 MHz, CDCl₃) : δ 121.3, 123.0, 129.2 (ArC), 144.7 (quatC) ppm.
Chapter Two

Synthesis of Substituted Guanidines

2.3.1.2 SYNTHESIS OF N,N',N''-TRI-(p-TOLYL)GUANIDINE

SYNTHESIS OF N,N'-DI-(p-TOLYL)THIOUREA 22

This was achieved by the following the literature conditions of Yamazaki, et al. 2

To a solution of p-toluidine (10.00 g, 93.3 mmol, 2 eq.) in DMF (100 cm³) cooled to 0°C, was slowly added diphenyl phosphite (93.3 mmol, 21.85 g, 17.86 cm³, 2 eq.). Care was taken to avoid a large exotherm and after the mixture had returned to 0°C, imidazole (93.3 mmol, 6.35 g, 2 eq.), followed by carbon disulphide (56 mmol, 4.26 g, 3.4 cm³, 1.2 eq.) were added and the mixture heated at 65°C for 4 hours. After cooling, the DMF was removed in vacuo and the residual liquid was treated with aqueous ethanol (50% v/v, 150 cm³) which afforded a yellow precipitate. This was collected by filtration and recrystallised from acetonitrile to yield a slightly yellow, microcrystalline solid (7.62 g, 64%), MP = 182°C (lit. 183°C); IR (nujol mull) \( \nu_{\text{max}} \) 3145(w) (N-H), 1589(m) & 1553(m) (C-N), 1142(s) (C=S) cm⁻¹; MS (+ve FAB) : [M+H]+ 257, 225 (M-S), 107, 91; Accurate mass, Found 257.11032; C₁₅H₁₆N₂S requires 257.11125; Deviation = -3.60 ppm; \(^1\)H NMR (250 MHz, DMSO) : \( \delta \) 2.28 (s, 6H, Me H), 7.13 (d, J=8 Hz, 4H, ArH), 7.35 (d, J=8 Hz, 4H, ArH), 9.63 (s, 2H, NH) ppm; \(^{13}\)C NMR (62.9 MHz, DMSO) : \( \delta \) 20.6 (CH₃), 124.0, 129.0 (Ar,CH), 133.7, 137.0 (Ar,quatC), 179.8 (C=S) ppm.

A larger scale synthesis of N,N'-di-(p-tolyl)thiourea was carried out on a 933 mmol scale and the product was obtained in a yield of 66.45 g (55%); MP = 179°C.

ATTEMPTED SYNTHESIS OF DI-(p-TOLYL)CARBODIIMIDE

The method reported by White and Mullin 2 was used to carry out this reaction.

A mixture of N,N'-di-(p-tolyl)thiourea 22 (7.8 mmol, 2.00 g) and lead(II) oxide (8.6 mmol, 1.92 g, 1.2 eq.) in distilled water (40 cm³) was refluxed for 18 hours, during which time the mixture darkened. After cooling the reaction mixture was filtered through celite to remove the lead residues, which were subsequently washed...
with DCM. The aqueous washings were extracted with DCM and the combined organic extracts were dried over Na$_2$SO$_4$ before the solvent was removed \textit{in vacuo}. The residual oil was taken up in a minimum volume of ether and any insoluble material was filtered off. The solvent was removed to yield a sticky oil (later solidifying) which showed no peak in the IR due to carbodiimide (N=C=N).

**Synthesis of Di-\((p\text{-tolyl})\)carbodiimide (Toluene Method)**

This was achieved by the method outlined by Ruby.$^{(2-7)}$

To a suspension of N,N'-di-(\(p\)-tolyl)thiourea 22 (7.8 mmol, 2.00 g) in toluene (20 cm$^3$), sodium chloride (0.14 g, 2.34 mmol, 0.3 eq.) in water (20 cm$^3$) was added, followed by sulphur (0.05 g, 0.2 eq.) and finally lead(II) oxide (1.91 g, 8.58 mmol, 1.1 eq.). This mixture was refluxed for 16 hours, cooled, then filtered through celite and washed with toluene (20 cm$^3$). The organic layer was separated and the aqueous layer further extracted with toluene (2 x 20 cm$^3$ aliquots). The combined organic extracts were dried over Na$_2$SO$_4$ and the solvent removed \textit{in vacuo}. The product was taken up in a minimum volume of ether and any insoluble material filtered off. The solvent was removed to yield a yellow oil (1.05 g, 61%). IR shows peak at 2108 cm$^{-1}$ due to carbodiimide but also one at 1640 cm$^{-1}$ from urea by-product. Recrystallisation from nhexane was attempted (removing any insoluble material) but the product would only form an oil (0.80 g, 46%); IR (thin film) $\nu_{\text{max}}$ 2108(s) (N=C=N) cm$^{-1}$; MS (+ve FAB): [M+H]$^+$ 223, 133, 118, 106, 91, 77; $^1$H NMR$^a$ (250MHz, CDCl$_3$): $\delta$ 2.33 (s, 6H, CH$_3$), 7.11 (s, 8H, ArH) ppm; $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$ 20.53 (CH$_3$), 112.59, 129.62 (Ar,CH), 132.45, 145.64 (Ar,quatC), 139.45 (N=C=N) ppm.

$^a$ Note:- There were also peaks in the NMR spectrum due to urea by-product, $^1$H: $\delta$ 2.37, 6.0, 7.14 ppm.

**ATTEMPTED SYNTHESIS OF DI-(p-tolyl)CARBODIIMIDE (ACETONE METHOD)**

This was performed by the procedure reported by Zetzsche and Nerger.$^{(2-8)}$

To a solution of N,N'-di-(\(p\)-tolyl)thiourea 22 (7.8 mmol, 2.00 g) in dry acetone (80 cm$^3$) under an atmosphere of nitrogen, sulphur (200 mg, 0.8 eq.) and lead(II) oxide (13.4 mmol, 3.00 g, 1.7 eq.) were added. The suspension was refluxed
for 8 hours during which time the colour darkened from yellow to black. An IR of this mixture showed no carbodiimide present so more sulphur was added (200 mg) and refluxed for a further 16 hours. An IR of the crude reaction mixture showed that carbodiimide was present. The mixture was filtered through celite and the solvent was removed. The residue was taken up in the minimum volume of ether and any insoluble material filtered off. The filtrate was cooled to -30°C which produced some more precipitate which was removed and finally, after removal of the ether, the residue was recrystallised from nhexane. The product was obtained as a yellow oil (1.29 g, 75%) which solidified on standing. IR (thin film) $\nu_{\text{max}}$ 2108 (N=C=N), 1645 (urea C=O) cm$^{-1}$.

This reaction was repeated on a similar scale as above except that more sulphur (1.00 g) was added from the start. Extreme care was also taken to exclude all traces of water from the starting materials and glassware. The reaction was set up and refluxed, under nitrogen, and the course of the reaction was followed by IR. However, even after 52 hours reflux there was no appreciable peak due to carbodiimide present in the spectrum.

FORMATION OF S-METHYL-DI-(p-TOYL)ISOThIURONIUM IODIDE FROM THE THIOUREA 23

This was done by adaptation of the method reported by Smidt and Andrieth.$^{(2-9)}$

To a suspension of N,N'-di-(p-tolyl)thiourea 22 (19.5 mmol, 5.00 g) in DME (20 cm$^3$), methyl iodide (23.4 mmol, 3.32 g, 1.5 cm$^3$, 1.2 eq.) was slowly added. The mixture was warmed to 40°C for 2 hours during which time a white solid formed. The solvent was removed then the residue was taken up into ether and the insoluble product was filtered off, washed with ether and dried to yield a white, microcrystalline solid (7.39 g, 95%); MS (+ve FAB) : [M-II$^+$ 271, 255, 223, 164, 149, 118, 106, 91, 77; $^1$H NMR (250 MHz, DMSO) : δ 2.32 (s, 6H, CH$_3$), 2.69 (s, 3H, SCH$_3$), 7.30 (s, 8H, ArH), 10.88 (br.s, 2H, NH) ppm; $^{13}$C NMR (62.9 MHz, DMSO), δ 14.90 (CH$_3$), 20.77 (SCH$_3$), 126.04, 130.11 (Ar,CH), 133.20, 137.93 (Ar,quatC), 169.03 (quatCS) ppm.

SYNTHESIS OF N,N',N''-TRI-(p-TOYL)GUANIDINIUM IODIDE

The reaction was conducted by the method first described by Rathke.$^{(2-10)}$

(a) Using DME as solvent
Toluidine (1.62 g, 15 mmol) was added, with stirring, to a suspension of S-methylisothiuronium iodide 23 (6.00 g, 15 mmol) in DME (50 cm³). This was warmed to 60°C for 3 hours after which time ¹H NMR analysis showed the presence of S-Me indicating that not all of the starting material had reacted. The mixture was then heated to reflux for 12 hours at which point all the solid had dissolved. The solvent was removed to leave a yellow oil and a crystalline product was obtained by trituration in ether with a few drops of DCM. The white solid was filtered off and dried (1.14 g, 17%) and found to be toludinium iodide; MS (+ve FAB): [M-I]⁺ 108; ¹H NMR (250 MHz, DMSO): δ 2.30 (s, 3H, CH₃), 7.26 (m, J=7 Hz, 4H, Ar,CH), 9.82 (br,s, 3H, NH₃) ppm; ¹³C NMR (62.9 MHz, DMSO): δ 20.69 (CH₃), 123.11, 130.37 (Ar,CH), 128.77, 137.93 (Ar,quatC) ppm.

(b) Using ethanol as solvent

To a suspension of the S-methylisothiuronium iodide 23 (1.00 g, 2.51 mmol) in dry ethanol (50 cm³), toluidine (0.27 g, 2.51 mmol) was added and the mixture was refluxed, under a nitrogen atmosphere, for 20 hours. After cooling, the ethanol was removed to leave a yellow oil which yielded a pale yellow solid upon trituration in ether (0.87 g) which was shown, by ¹H NMR spectroscopy, to be unreacted starting material.

SYNTHESIS OF DI-(p-TOLYL)CARBODIIMIDE 24

Following the literature method of Appel, et al, (2-13) N,N'-di-(p-tolyl)thiourea 22 (7.8 mmol, 2.00 g), triphenylphosphine (7.8 mmol, 2.05 g), triethylamine (7.8 mmol, 0.79 g, 1.09 cm³) and carbon tetrachloride (7.8 mmol, 1.20 g, 0.75 cm³) were washed into a flask with DCM (20 cm³). The mixture was heated to 40°C and after 1 hour had resulted in a clear yellow solution. After a further 2 hours some solid had formed and the reaction was cooled. The solvent was removed, then the product was extracted from the residue by washing with nhexane then ether. After cooling at -30°C overnight the ether solution was filtered and the solvent removed to yield an orange oil (1.07 g, 62%) which crystallised on standing. NMR of this product shows phenyl impurity which may be due to triphenylphosphine or triphenylphosphinesulphide. The
product was purified further by distillation at 200°C / 1mmHg to yield a yellow oil 0.52 g, 30%; IR (thin film) ν_max 2142, 2109(s) (N=C=N) cm⁻¹; ^1H NMR (250 MHz, CDCl₃) : δ 2.37 (s, 6H, CH₃), 7.13 (m, 8H, Ar,H) ppm; ^13C NMR (62.9 MHz, CDCl₃) : δ 20.80 (CH₃), 123.75, 129.89 (Ar,CH), 128.38, 133.40 (Ar,quatC), 135.61 (N=C=N) ppm.

Note:- Additional peaks in NMR due to presence of PPh₃ S, i.e. δ_C 128-135 ppm.

**SYNTHESIS OF N,N',N''-TRI-(p-TOLYL)GUANIDINE 25**

Again the method of Mikolajczyk, *et al.*, was adapted for this reaction.

Di-(p-tolyl)carbodiimide 24 (0.5 g, 2.25 mmol) and toluidine (2.75 mmol, 0.27 g, 1.1 eq.) in dry toluene (20 cm³) were refluxed for 20 hours. After cooling, the solvent was removed to leave a dark yellow oil which was recrystallised from di-isopropylether to yield white crystals which were filtered off, washed with cold nhexane, then dried. The product was obtained in a yield of 0.57 g (76%), MP = 123°C; CHN: C₇₂H₷₃N₃ requires C 80.20, H 7.05, N 12.82; Found C 80.36, H 7.17, N 12.79; IR (nujol mull) ν_max 3385(m) (N-H), 1644(s) (C=N) cm⁻¹; MS (+ve FAB) : [M+H]⁺ 331, 222; Accurate mass, Found 329.18864; C₇₂H₷₃N₃ requires 329.18920; Deviation = -1.69 ppm; ^1H NMR (250 MHz, CDCl₃) : δ 2.32 (s, 9H, CH₃), 5.80 (br,s, 2H, NH), 7.11 (s, 12H, Ar,CH) ppm; ^13C NMR (62.9 MHz, CDCl₃) : δ 20.62 (CH₃), 121.58 (br, Ar,quatC), 129.72 (Ar,CH), 145.34 (quatC) ppm.

The synthesis of the guanidine was repeated on a 0.19 mol scale and the thiourea was converted to the carbodiimide without purification. Reaction of this carbodiimide with p-toluidine produced the crude guanidine which was purified as follows. Excess toluidine was removed by distillation but the product would not crystallise from di-isopropylether due to the large amount of triphenylphosphinesulphide impurity remaining. This was removed by column chromatography (silica, 100 g). Triphenylphosphinesulphide obtained when eluted with 50:50 nhexane/ether while the product was collected by elution with 50:50 ether/ethyl acetate. The product fractions were combined, solvent removed and finally recrystallised from di-isopropylether to yield a white microcrystalline solid which was
washed with cold nhexane. The product was obtained in a yield of 23.62 g (38\% from N,N'-di-(p-tolyl)thiourea); MP = 121°C. Spectroscopic analysis of the product was in agreement with the previously synthesised tri-(p-tolyl)guanidine.

**PREPARATION OF N,N',N''-TRI-(p-TOLYL)GUANIDINIUM HYDROCHLORIDE**

N,N',N''-tri-(p-tolyl)guanidine 25 (0.5 g, 1.52 mmol) was dissolved in ethanol (20 cm$^3$) then hydrochloric acid (1.52 mmol, 1.52 cm$^3$ 1M) was slowly added with stirring. After 30 minutes the solvent was removed and traces of water were removed by repeated dissolving in ethanol and evaporating solvent. This was repeated 3 times using ether to leave a white powder (0.39 g, 70\%); MP = 233-234°C.

2.3.1.3 **SYNTHESIS OF TRI-TERT-BUTYLGUANIDINE 26**

The procedure followed in this reaction has been described by Chivers *et al.*

To a solution of tert-butylamine (3.00 g, 41 mmol, 4.33 cm$^3$, 1.5 eq.) in dry THF (20 cm$^3$) at -78°C, was added "BuLi (2.5M in hexanes, 17.2 cm$^3$, 43 mmol, 1.57 eq.). The resulting mixture was stirred at -78°C for five minutes then allowed to warm to room temperature and stirred for thirty minutes. The mixture was recooled to -78°C and added via cannula to a solution of di-tert-butylcarbodiimide (4.22 g, 27.3 mmol, 5.27 cm$^3$) in dry THF (20 cm$^3$) at -78°C. The resulting mixture was allowed to warm slowly to room temperature whereupon some of the white precipitate dissolved and a very pale green solution formed. Warming to 50°C for fifteen minutes caused dissolution of the mixture and a pale yellow solution to form. After the solution cooled to room temperature, water (50 cm$^3$) was added dropwise to the rapidly stirred solution causing a white precipitate to form. The reaction mixture was extracted with ether (2 x 50 cm$^3$) and the combined organic fractions washed with water (2 x 25 cm$^3$), dried over MgSO$_4$, filtered and evaporated in vacuo to yield a pale yellow oil. This was purified by Kugelrohr distillation at 100-110°C / 12 mmHg (lit. 95-96°C / 11 mmHg) to yield a colourless oil (3.82 g, 62\%); IR (thin film): $\nu_{max}$ 3454 (m) (N-H), 1651 (s) (N=C) cm$^-1$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 1.26 (br, s, 27H, C(CH$_3$)$_3$) ppm; $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$ 29.28, 30.93, 31.22, 31.73 (C(CH$_3$)$_3$), 49.96 (CMe$_3$), 146.77 (quatC) ppm.
2.3.1.4 *Synthesis of N,N',N''-tris((s)-(-)- α – methylbenzyl)guanidine* 27

The outline for this experiment was described by Mikolajczyk, *et al.*\(^{(2-2)}\)

To a solution of bis((s)-(-)-α–methylbenzyl)carbodiimide (2 g, 8 mmol) in dry diglyme (10 cm³) was added ((s)-(-)-α–methylbenzyl)amine (1.07 g, 1.13 cm³, 8.8 mmol, 1.1 eq.). The resulting mixture was heated, under nitrogen, for eighteen hours at 120°C. Infra red spectroscopy of a concentrated aliquot showed very little carbodiimide and a peak at 1638 cm⁻¹. After cooling the solvent was removed by co-distillation with xylenes (four times) followed by toluene (twice). Remaining solvent removed *in vacuo* to yield a viscous orange oil. This was dissolved in ether and filtered to remove white precipitate (bis((s)-(-)-α–methylbenzyl)urea). Attempts to crystallise the oil from mixtures of DCM, ether and nhexane failed. Solvents were removed to dryness to yield an orange oil (2.72 g, 91%) which crystallised during storage in the fridge; *IR* (thin film): \(\nu_{\text{max}}\) 3431 (m) (N-H), 1640 (s) (N=C) cm⁻¹; *MS* (+ve EI): \([M+H]^+\) 371, 251, 171; Accurate mass, Found 371.23637; \(\text{C}_{25}\text{H}_{29}\text{N}_3\) requires 371.23615; Deviation = 0.60 ppm; \(^1\text{H NMR}\) (250 MHz, CDC\(_3\)): \(\delta\) 1.37 (d, \(J = 6.6\) Hz, 9H, -C(Ph)H-CH\(_3\)), 4.57 (q, \(J = 6.6\) Hz, 3H, -C(Ph)H-CH\(_3\)), 6.78-6.83 (m, 6H, ArH), 7.15-7.23 (m, 9H, ArH) ppm; \(^{13}\text{C NMR}\) (62.9 MHz, CDC\(_3\)): \(\delta\) 24.96 (-C(Ph)H-CH\(_3\)), 52.21 (-C(Ph)H-CH\(_3\)), 125.81, 126.19, 128.07 (ArC), 146.23 (ArquatC) 149.19 (quatC) ppm.

*S Synthesis of N,N',N''-tris((s)-(-)- α – methylbenzyl)guanidinium hexafluorophosphosphate* 28

To a solution of N,N',N''-tris((s)-(-)-α–methylbenzyl)guanidine 27 (1 g, 2.70 mmol) in EtOH (20 cm³) cooled to 0°C, was added hexafluorophosphoric acid (60% wt. solution in H\(_2\)O, 0.66 cm³, 2.71 mmol). The resulting solution was allowed to warm to room temperature then the solvent was removed *in vacuo* then co-distilled with EtOH (three times) to remove water. The residue was taken up in ether, filtered, washed with ether and dried to yield a white solid (0.96 g, 69%). Crystals suitable for X-ray study were grown by slow evaporation of an EtOH / EtOAc solution; \text{CHN} : \(\text{C}_{25}\text{H}_{30}\text{N}_3\text{PF}_6\) requires C 58.02, H 5.80, N 8.12; Found C 58.41, H 6.14, N 7.96; *IR*
Chapter Two

Synthesis of Substituted Guanidines

(nujol mull): \( \nu_{\text{max}} \): 3417 (s) (N-H), 1620 (s) (N=C) cm\(^{-1}\); \textbf{MS} (+ve FAB): \([M+H^+\text{-PF}_6]\)

372, 268, 251, 193; Accurate mass, Found 372.24355; \( C_{25}H_{30}N_3 \) requires 372.24397; Deviation = -1.15 ppm; \(^1\)H NMR (250 MHz, d\(_6\)-DMSO): \( \delta \) 1.38 (d, \( J = 6.6 \) Hz, 9H, -C(Ph)H-CH\(_3\)), 5.09 (q, \( J = 6.6 \) Hz, 3H, -C(Ph)H-CH\(_3\)), 6.59-6.62 (m, 6H, ArH), 7.03-7.24 (m, 9H, ArH), 7.51 (d, \( J = 5.7 \) Hz, 3H, -NH) ppm; \(^{13}\)C NMR (62.9 MHz, d\(_6\)-DMSO): \( \delta \) 22.95 (-C(Ph)H-CH\(_3\)), 50.70 (-C(Ph)H-CH\(_3\)), 125.88, 127.20, 128.52 (ArC), 142.88 (ArquatC) 152.87 (quatC) ppm.

\textit{Crystal data for 28.}

Data were collected on a Stoe Stadi4 diffractometer using a colourless block of dimensions 0.33 x 0.23 x 0.19 mm using the \( \omega-\theta \) method in the range 3\(^\circ\) \( \leq \theta \leq 60^\circ\). The structure was solved by direct methods (SIR 92).\(^{(2-15)}\) Of the two molecules in the unit cell one guanidine was ordered on a site of 3\(^2\) symmetry, the others was disordered about a 32 site. The PF\(_6^+\) was ordered on a 2 site. The hydrogen atoms were placed in calculated positions and anisotropic displacement parameters were refined for all other atoms, giving a final \( R \) of 0.0639 for 204 parameters. The final difference map extrema were 0.294 and -0.392 e\( \cdot \)A\(^3\).

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C(<em>{25})H(</em>{30})F(_6)N(_3)P</th>
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<th>120</th>
</tr>
</thead>
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<td>Volume / A(^3)</td>
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<td>Crystal system</td>
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<td>Z</td>
<td>6</td>
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<td>Space group</td>
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<td>Wavelength / A</td>
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<tr>
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<td>( \beta / ^\circ )</td>
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<td>( wR_2 ) (all data)</td>
<td>0.1632</td>
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\textit{Table 2.2 Crystallographic Data for 28.}
2.3.2 SYNTHESIS OF TETRASUBSTITUTED GUANIDINE

SYNTHESIS OF N,N-DIETHYL-N',N' '-DIPHENYLGUANIDINE 29

This was also prepared using the method of Mikolajczyk, et al.\(^{(2-2)}\)

To a solution of diphenylcarbodiimide (11.27 g, 58 mmol) in toluene (250 cm\(^3\)) was added freshly distilled diethylamine (6 cm\(^3\), 58 mmol). After 20 hours of heating under reflux the solvent was removed by rotary evaporation. The residual white precipitate was recrystallised from toluene and \(n\)hexane (50:50) to yield fluffy, white crystals (9.68 g, 62%); \(\text{MP} = 93-94^\circ\text{C}\); \(\text{CHN} : \text{C}_{17}\text{H}_{21}\text{N}_3\) requires C 76.4, H 7.9, N 15.7; Found C 76.59, H 7.97, N 15.89; \(\text{IR (nujol mull): } \nu_{\text{max}} 3150 \text{ (m) (N-H), 1609 \text{ (w) (N=C) cm}^{-1}}; \text{MS (+ve FAB): } [\text{M+H}]^+ 268, 238, 195, 175, 119, 93; \text{Accurate mass, Found 268.18251; } \text{C}_{17}\text{H}_{21}\text{N}_3\) requires 268.18137; Deviation = 4.25 ppm; \(\text{\textsuperscript{1}H NMR (250 MHz, CDCl}_3): } \delta 1.16 \text{ (t, } J = 7.1 \text{ Hz, 6H, -CH}_2\text{-CH}_3\text{), 3.33 (q, } J = 7.1 \text{ Hz, 4H, -CH}_2\text{-CH}_3\text{), 5.40 (br, s, 1H, NH), 6.86-6.96 (m, 6H, ArH), 7.18-7.25 (m, 4H, ArH) ppm; } \text{\textsuperscript{13}C NMR (62.9 MHz, CDCl}_3): } \delta 12.7 \text{ (-CH}_2\text{-CH}_3\text{), 41.8 (-CH}_2\text{-CH}_3\text{), 118.49, 121.7, 129.0 (ArC), 150.0 (quatC) ppm.}
2.4 REFERENCES

CHAPTER THREE

MONODENTATE GUANIDINE LIGANDS

3.1 INTRODUCTION

As was outlined in the introduction, there are a number of complexes characterised that contain a monodentate guanidine ligand, though in the majority of these the guanidine is tetramethylguanidine. However, in comparison to the number of complexes known which contain a monoanionic amidinate ligand, monodentate complexes of neutral amidines are rare. The first examples of monodentate amidine complexes were synthesised by Bradley and Wright in 1956. It is common for monodentate amidine complexes to only form when the coordination number of the metal is low or if a polydentate ligand is already bound to the metal centre restricting coordination of the amidine. This is the case when using the 2,6-bis[(dimethylamino)methyl]phenyl ligand (bdmp) in the starting complex, \([\text{M(bdmp)}(\text{H}_2\text{O})][\text{BF}_4]\), \(\text{M=}\text{Pd, Pt}\), and reacting it with di-(p-tolyl)formamidine (Hdptf) in acetone. The resulting cationic complex, \([\text{M(bdmp)}(\text{Hdptf})]^+\) (Fig. 3.1), formed by substitution of the labile H2O ligand, has the formamidine bound through its imine nitrogen (N1) alone. This is because the metal has already obtained its preferred square planar geometry and three of the coordination sites are filled with the rigid (bdmp) ligand. Deprotonation of the acidic amine (N2) generates the neutral, covalent complex, \([\text{M(bdmp)}(\text{dptf})]\), which is bound through the former imine nitrogen (N1).

Further examples of monodentate amidine complexes are the divalent metal chloride amidines studied by Cotton and co-workers. These complexes were
Chapter Three

Monodentate Guanidine Ligands

synthesised by solubilising metal chlorides with amidines in toluene solution and have been used as precursors to dimeric metal complexes. Monodentate complexes of this type have been characterised containing Mn, Fe, Co, Ni, and Pt metal centres and some of these will be discussed later.

Also relevant to this work is a recent paper describing the formation of a three-coordinate silver complex which contains two neutral formamidine ligands. This was published while the silver reactions were under study.

While the work on silver complexes described in this chapter is my own the cobalt complexes were synthesised by Lisa J. Stewart, an Honours project student working under my supervision. The complexes discussed in this chapter which were fully characterised were the subject of a recent publication.

3.2 REACTION OF SILVER(I) SALTS WITH GUANIDINES

It was hoped that the reaction of silver(I) trifluoromethanesulphonate $[\text{AgSO}_3\text{CF}_3]$, also known as silver(I) triflate $[\text{AgOTf}]$, with guanidines would yield complexes containing neutral guanidine ligands binding through their imine nitrogen. The initial strategy for these reactions was to dissolve silver triflate in acetonitrile to form the $[\text{Ag(MeCN)}_2]^+$ cation. It was anticipated that addition of guanidine, a stronger donor, would substitute the labile acetonitrile ligands providing the desired monodentate guanidine complexes. This was attempted without initial success, then Cotton’s silver formamidine paper was published and the reaction was attempted by this method, i.e. refluxing in toluene, which ultimately proved successful. Finally, due to the difficulty in crystallising the tris((s)-(-)-$\alpha$-methylbenzyl)guanidine complex as the triflate salt, the reaction was tried using silver(I) tetraphenylborate $[\text{AgBPh}_4]$, the rationale being that the bulkier tetraphenylborate anion would allow better packing of the ions, so promoting crystallisation.

3.2.1 REACTION OF SILVER(I) TRIFLATE IN ACETONITRILE

Silver(I) triflate was found to be readily soluble in acetonitrile, giving rise to a colourless solution. Addition of two molar equivalents of triphenylguanidine
caused an immediate brown colour to form at room temperature. After stirring for two hours, addition of ether caused a fine, pale precipitate to form though attempts to crystallise this from acetonitrile / ether mixtures failed.

Although no further reactions were attempted in this manner, it is likely that an alkyl substituted guanidine would be more effective at displacing the acetonitrile ligands, simply due to the fact that it would be a stronger donor than a guanidine with aryl substituents.

### 3.2.2 Reactions of Silver(I) Triflate in Toluene

These reactions were carried out following the procedure described by Cotton, *et al.* In the reaction with two equivalents of triphenylguanidine, addition of toluene dissolved most of the solid, then the mixture was refluxed for one hour. A pale coloured solution formed though a silver mirror also formed on the walls of the Schlenk. Filtration gave a pale pink solution which was dried *in vacuo* yielding a pale pink solid. Crystals 31 were obtained by dissolving the solid in the minimum volume of toluene and layering with hexane. The low yield is probably due to some decomposition of the silver salts (starting material or product) as evidenced by the formation of a silver mirror of the walls of the glassware.

The infrared spectrum of this as a nujol mull showed a shift in the imine stretching frequency from the free guanidine (1635 → 1618 cm⁻¹). Previous studies of transition metal guanidine complexes have shown a similar reduction in C=N stretching frequency. Thus, a low energy shift of these 1,1,3,3-tetramethylguanidine complexes was interpreted as indicating coordination through the imine rather than an amine nitrogen. The v(N-H) modes of 31 are seen as two sharp absorptions at 3366 and 3304 cm⁻¹. The ¹H and ¹³C NMR spectra are very similar to the free ligand, the only differences being shifts in the peak for NH protons from 5.9 to 7.4 ppm and the signal for the central CN₃ carbon from 144.7 to 152.7 ppm. The shift for this carbon is consistent with coordination to a metal as loss of electron density, through coordinate bond formation, lessens the shielding of the carbon nucleus resulting in an increase in its chemical shift. The positive ion FAB mass spectrum has a peak at m/z 684 corresponding to the molecular ion.
[Ag{PhN=C(NHPh)₂}₂]⁺ and peaks arising from loss of triphenylguanidine (394), triphenylguanidine itself (288) and diphenylcarbodiimide (194). From this spectroscopic evidence, it was concluded that the isolated product did contain neutral triphenylguanidine ligands though the coordination geometry at silver was unknown. In particular, the solubility of the complex in toluene indicated that the species was neutral, i.e. the complex does not exist as discrete ions. One possibility would be that the triflate ion could be bound to the silver atom, resulting in a three coordinate complex, similar to the silver formamidine complex previously characterised.⁶ An X-ray crystal structure determination was undertaken in order to determine the coordination environment of the silver ion as well as the overall structure of the complex.

The crystals of 31 were found to contain two independent molecules per unit cell consisting of a linear [Ag{PhN=C(NHPh)₂}₂]⁺ complex with an associated triflate counter ion. One molecule from the unit cell is shown (Fig. 3.2) with two associated triflate counter ions and selected bond lengths and angles are listed (Table 3.1). Both molecules possess an inversion centre at silver which relates the two ligands and though there are some differences in the metrical parameters, only those pertaining to the molecule containing Ag(1) are discussed here. As it must be, the geometry at silver is perfectly linear [N(11)-Ag(1)-N(11a) 180°] with the triflate ion not coordinated to the silver atom. In fact, triflate ions were found to be hydrogen bonded via S=O oxygens to the amino hydrogens on the uncoordinated nitrogens. This accounts for the solubility of the complex in toluene as the hydrogen bonding effectively creates a “neutral” molecule. The N-O distances in these N-H···O systems range from 2.912(12) to 3.109(13) Å and the N-H-O angle from 128.5 to 145.3°.

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Angle (°)</th>
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<td>Ag(1)-N(11)</td>
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</tr>
<tr>
<td>N(11)-Ag(1)-N(11a)</td>
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</tr>
<tr>
<td>C(11)-N(11)</td>
<td>1.32(1)</td>
</tr>
<tr>
<td>N(11)-C(11)-N(21)</td>
<td>120.7(8)</td>
</tr>
<tr>
<td>C(11)-N(21)</td>
<td>1.36(1)</td>
</tr>
<tr>
<td>N(11)-C(11)-N(31)</td>
<td>125.7(8)</td>
</tr>
<tr>
<td>C(11)-N(31)</td>
<td>1.36(1)</td>
</tr>
<tr>
<td>N(21)-C(11)-N(31)</td>
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</tr>
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<td>O(30)-N(21)</td>
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<td>N(21)-H(21)-O(30)</td>
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<td>2.912(12)</td>
</tr>
<tr>
<td>N(31)-H(31)-O(30)</td>
<td>145.3</td>
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</table>

Table 3.1. Selected bond lengths (Å) and angles (°) for 31.
Figure 3.2. X-ray crystal structure of $[\text{Ag}(\text{PhN}=\text{C(NHPh)}_2)]^+$ showing two hydrogen-bonded $\text{SO}_3\text{CF}_2^-$ groups.
The Ag-N distance in the complex \([\text{Ag}(1)-\text{N}(11) 2.135(8) \text{ Å}]\) is intermediate between those found for the bis(ammine) complex \([\text{Ag(NH}_3)_2][\text{ClO}_4] [2.112(6) \text{ and } 2.117(6) \text{ Å}]^{3(11)}\) and the polymeric ethylenediamine complex \([\{\text{Ag(en)}\}_n][\text{ClO}_4]_n [2.17(1) \text{ Å}]^{3(12)}\), both of which exhibit essentially linear coordination of the silver ion.

The crystal structure also confirms that the guanidine ligands are bound through their imine nitrogens. Though the amine hydrogens were not directly located, comparison of the C-N distances in the central CN_3 unit of the guanidine ligand reveal that it is the imine nitrogen, N(11), which coordinates to the metal centre \([\text{C}(11)-\text{N}(11) 1.32(1), \text{C}(11)-\text{N}(21) 1.36(1), \text{C}(11)-\text{N}(31) 1.36(1) \text{ Å}]\).

In terms of the ligands the most closely related structurally characterised complex is the silver formamidine complex \([\text{Ag(PhN=CH-NHPh)}_2-\text{(O}_3\text{SCF}_3)]\) in which the Ag-N distances \([2.179(4) \text{ and } 2.206(4) \text{ Å}]\) are significantly longer than those in 31.(3-6) Although in both complexes the silver is coordinated by Ph-N=C imine nitrogen atoms, the differences in Ag-N distances may be attributed to the difference in geometry of the silver centre. This variation in coordination geometry is surprising as neutral formamidine and guanidine ligands would be expected to have similar donor properties. This suggests, therefore, that the contrast in geometry must be steric rather than electronic in origin. Indeed, the presence of the third NHPh group in the guanidine (versus H for the formamidine) is crucial as it is clear in the structure of 31 that the silver is shielded from further coordination by two flanking phenyl groups on uncoordinated nitrogens.

The structure of 31 is similar to the tetramethylguanidine gold(I) halide complexes reported by Schmidbaur et al (page 11).(3-13) These complexes exist in equilibrium in solution though in the solid state they form ionic pairs with long Au···Au contacts. The cation \([\text{Au}\{\text{NH} = \text{C(NMe}_2)_2\}_2]^+\), in which the gold is coordinated by two neutral guanidine ligands, has almost linear geometry \([\text{N-Au-N} 178.8(5)°]\). The guanidine ligands were found to coordinate through their imine nitrogens (low energy shift of imine stretch) and the two coordinate bonds are equal within one standard deviation \([\text{Au-N(1) 2.006(9) Å, Au-N(4) 1.993(9) Å}]\).
REACTION WITH TRI-(TERT-BUTYL)GUANIDINE

The reaction was repeated under similar conditions using two equivalents of tri-(tert-butyl)guanidine. A silver mirror formed on the walls of the Schlenk while refluxing and an off-white solid was again obtained after drying the filtrate of the reaction mixture. However, in addition to the solid, a colourless oil also remained and the infrared spectrum of the residue showed $\nu$(C=N) mode at 1650 cm$^{-1}$ with a shoulder at 1600 cm$^{-1}$, indicating the presence of free and bound guanidine ligand. Following washing with hexane, the infrared spectrum of the solid had only one band [1600 cm$^{-1}$] while the hexane washings also showed only one band [1650 cm$^{-1}$]. This indicated that the off-white solid (230 mg, 24%) 32 obtained from the reaction was free from non-complexed guanidine ligand. Therefore, a low energy shift of 45 cm$^{-1}$, similar to the previous triphenylguanidine complex is observed, indicating that the guanidine is again coordinating through its imine nitrogen to the silver ion. The infrared spectrum of the solid also shows a broad band at 3341 cm$^{-1}$ from the $\nu$(N-H) modes and a strong, sharp band at 1032 cm$^{-1}$ from the $\nu$(C-F) stretch.

The $^1$H and $^{13}$C NMR spectra of the solid also show significant changes which occur as a result of coordination of the ligand. The $^1$H NMR shows a very large singlet that is not broadened as the corresponding peak in the free guanidine is. A peak for the NH protons is also observed, although this is smaller than expected, probably as a result of hydrogen exchange of these acidic protons with the deutero-chloroform. This can be inferred as a correspondingly large signal is observed for the chloroform (though no signal is observed from water in the solvent which would also result in exchange of the deuterium from the chloroform).

In the $^{13}$C NMR spectrum of the free ligand, four distinct signals were observed for the methyl carbons (a result of steric hindrance preventing free rotation of 'Bu groups - page 45) whereas in 32 only one peak is observed for those carbons. This is a surprising observation as it would be expected that complexation of the guanidine to the silver would merely increase the steric hindrance within the molecule. There are a few plausible explanations for this effect although no firm experimental evidence is available on which to form a conclusion. However, based on the fact that only single sharp peaks are observed in the spectrum, it would appear
that complexation of the silver actually promotes internal exchange of the imine bond within the guanidine framework, thus making all resonances appear equivalent on the NMR timescale. This offers an explanation for the observed spectra, though by what mechanism this would occur remains unclear. Also of significance is the shift from 146.8 → 152.4 ppm for the central CN₃ carbon. This downfield shift is indicative of a reduction in electron density at this carbon arising from electron donation of the imine nitrogen to the silver ion.

The positive ion FAB mass spectrum of 32 shows no peak at \( m/z \) 562 from the anticipated product. In fact the highest peak observed in the spectrum occurs at \( m/z \) 228, corresponding to the free ligand. This would suggest that the complex is not particularly robust, more than likely as a result of the steric strain present within the molecule.

These results suggest that a complex containing neutral guanidine ligands has formed, though it was only obtained in poor yield. The comparatively low yield of the complex almost certainly results from the increased steric bulk of the \('Bu\) groups preventing complexation of the imine nitrogen to the silver. The low yield is also evident from the fact that unreacted ligand is isolated from the reaction mixture.

**REACTION WITH TRICYCLOHEXYLGUANIDINE**

In the knowledge that reactions between guanidines and silver triflate proceed at reflux in toluene, the reaction with tricyclohexylguanidine was attempted at room temperature. This was to test whether an alkyl substituted guanidine would be a strong enough donor to complex the metal without the need to heat the mixture. This is somewhat similar to the first reaction attempted in acetonitrile except that in this case the toluene will not coordinate to the silver. This may be of advantage as displacement of ligated acetonitrile will not be necessary in order for the guanidine to bind. Unfortunately the silver triflate will not be as soluble in toluene as acetonitrile, though it should still be soluble enough for it to react.

The reaction was carried out by the same method as previously described except that the mixture was maintained at room temperature and not heated to reflux. Solution infrared was used to follow the reaction, the main indication of complex
formation being the expected low energy shift for the $\nu(\text{C}=\text{N})$ mode. The spectra were somewhat complicated by the presence of a band at 1604 cm$^{-1}$ from $\nu(\text{C} \cdot \text{C})$ in toluene though $\nu(\text{C}=\text{N})$ for the guanidine was initially observed at 1620 cm$^{-1}$ in toluene. After addition of silver triflate, the infrared was measured over a period of twenty-four hours though no change was observed for $\nu(\text{C}=\text{N})$. The only physical change observed was the formation of some brown precipitate in the reaction flask, though the solution remained colourless. No attempt was made to isolate any product as there was no evidence that any reaction had occurred.

**REACTION WITH TRIS((S)-(-)α-METHYLBENZYL)GUANIDINE**

Owing to the lack of success of the reaction with tricyclohexylguanidine at room temperature, the reaction with two equivalents of tris((S)-(-)α-methylbenzyl)guanidine was undertaken at reflux. The reaction proceeded in a similar manner to those previous; a silver mirror forming on the walls of the Schlenk and a cream coloured solution obtained after filtration. However, removal of the solvent left an oily, yellow product as opposed to a solid as anticipated. This though, was thought to be due to residual toluene and attempts were made to crystallise the product from toluene and toluene / hexane mixtures. These proved unsuccessful as it appeared that the product was indeed an oil which only solidified upon cooling. In an attempt to synthesise a more crystalline product, the reaction was attempted with silver(I) tetraphenylborate as it was hoped that the bulkier counter anion would promote the formation of a crystalline product.

**3.2.3 REACTION OF SILVER(I) TETRAPHENYLBORATE**

The reaction was carried out in the same method for the triflate salt except that acetonitrile was used as the solvent, due to the complete insolubility of AgBPh$_4$ in toluene. After refluxing the mixture for one hour under a nitrogen atmosphere, filtration isolated a black solid from a colourless filtrate. Drying of the filtrate revealed that the filtrate consisted of solvent alone, as no involatile material remained. The black solid (first thought to be silver oxide) must be a product of decomposition, either of AgBPh$_4$ or, more likely, a silver guanidine complex (as no
free guanidine remained in the filtrate). The insolubility of this solid in organic solvents suggested that it was not a complex containing a guanidine ligand so recrystallisation was not attempted.

Hence, the change in counterion was unsuccessful with the product either not forming at all, or decomposing under reaction conditions. Either way, it was not possible to obtain crystals suitable for X-ray study of a complex containing the chiral substituted guanidine which was the reason for changing the counter-ion in the first instance.
3.3 REACTIONS OF COBALT(II) CHLORIDE WITH GUANIDINES

The reactions of cobalt(II) chloride with guanidines were studied as part of a project with the ultimate goal of synthesising guanidinate bridged metal dimers. Initially it was hoped that reaction of guanidines with transition metal halides would yield complexes with the guanidine acting as a neutral donor (Fig. 3.3). These complexes would then be used as precursors to metal dimers, treatment with strong base eliminating HCl and providing the guanidinate bridged systems.

Analogous reactions with amidines had been reported\(^{(3-14,3-5)}\) whereby reaction with transition metal halides produced tetrahedral complexes of the formula \([\text{ML}_2\text{X}_2]\) (where \(\text{L} = \text{neutral amidine}\)). Deprotonation of these systems with MeLi lead to formation of the dimeric species bridged by amidinate ligands.\(^{(3-14,3-15)}\)

It was anticipated that guanidines would behave in much the same manner as amidines and synthesis of analogous complexes with guanidine based ligands was attempted in the course of the project. In order to have access to the metal dimers, routes to complexes containing the neutral ligands were required. The reactions of cobalt(II) chloride with triphenylguanidine are discussed herein.

3.3.1 REACTION IN TOLUENE

The initial attempt at this reaction followed the procedure Cotton, et al described for the synthesis of \([\text{CoCl}_2(\text{HDPhBz})_2]\) (HDPhBz = diphenylbenzamidine).\(^{(3-5)}\) An excess of anhydrous cobalt(II) chloride and triphenylguanidine were refluxed in toluene for twenty-four hours. During this time the solution deepened in colour though after filtration and cooling the solution lost
much of its colour and unreacted CoCl$_2$ precipitated. It was clear that no reaction had occurred so the reaction was attempted in THF, with the view that increasing the solubility of the CoCl$_2$ would promote reaction with the guanidine.

### 3.3.2 Reaction in THF

Upon addition of THF to the mixture of CoCl$_2$ and guanidine a bright blue solution formed, clearly indicating the enhanced solubility of the CoCl$_2$ in this solvent. Reflux of this mixture, under nitrogen, for twenty-four hours provided a bright blue solution from which X-ray quality crystals were obtained from a slowly evaporated DCM / hexane solution. Unfortunately the yield of the product was low, so the reaction was repeated on a larger scale and the mixture was heated for a longer period (eighty-nine hours). Crystals 33 were obtained from this reaction in a similar manner, though in a much improved yield (77%).

The infrared spectrum of these crystals again showed a low frequency shift for the $\nu$(C=N) band [1635 $\rightarrow$ 1626 cm$^{-1}$], though this was less marked than for 31. A difference was also noted for the $\nu$(N-H) modes which appeared as a broad band at 3351 cm$^{-1}$ compared to a sharp band at 3347 cm$^{-1}$ in the free ligand. Further evidence for the formation of a bis(guanidine) complex was gained from FAB mass spectrometry in which a peak was observed for the parent ion at $m/z$ 704.

A crystal structure determination confirmed that 33 was [CoCl$_2$(PhN=C(NHPh)$_2$)$_2$], a tetrahedral complex in which the Co(II) ion is ligated by two chloride ions and two neutral guanidine molecules. The unit cell consists of two independent molecules of 33, solvated by two molecules of DCM. The difference in bond lengths between the molecules is not crystallographically significant though bond angles differ markedly. The differences encountered in these angles were believed to be a result of the effects of crystal packing of the molecules and not as a result of any chemical difference. The molecular structure of 33 is shown (Fig. 3.4) and tables of selected bond lengths (Table 3.2) and angles (Table 3.3) for the molecule containing Co(1) are provided.
Figure 3.4. X-ray crystal structure of $[\text{Co(PhN=C(NHPh)_2Cl}_2]_{33}$.

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<tr>
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<td>Co(1)-Cl(2)</td>
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<td>C(11)-N(21)</td>
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<td>C(11)-N(31)</td>
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<td>1.361(8)</td>
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</table>

Table 3.2. Selected bond lengths (Å) for $[\text{Co(PhN=C(NHPh)_2Cl}_2]_{33}$.}

---

Page 73
The geometry at the Co(II) centre is only slightly distorted from tetrahedral, the angle defined by the two nitrogen ligands being somewhat larger [N(11)-Co(1)-N(12) 113.2°] and for the two chlorides correspondingly smaller [Cl(l1)-Co(l)-Cl(21) 105.32(8)°]. In the benzamidine complex, the N-Co-N angle is similar [112.8(2)°] though for Cl-Co-Cl the angle is much larger [111.06(6)°]. However, comparison of the angles of the second molecule of 33 [N-Co(2)-N 108.1(2) and Cl-Co(2)-Cl 107.35(8)°] suggest that the discrepancies in the bond angles are not a result of any significant chemical difference imposed by the guanidine compared to the amidine ligands.

While not being exactly symmetrical, the coordinate bonds in 33 show no significant variation in length [av. Co(1)-N 2.014 and Co(1)-Cl 2.282 Å]. The lengths of corresponding bonds in the benzamidine and formamidine complexes do not show an appreciable difference [ca. 0.01 Å longer for Co-N and 0.01 Å shorter for Co-Cl] again indicating the similarity between the neutral amidine and guanidine ligands. However, compared to the complexes [CoCl₂(NC₅H₄OMe-2)₂] and [CoCl₂(NC₅H₄Me-4)₂] the Co-N bonds in 33 are 0.05 Å shorter while the Co-Cl bonds in 33 are 0.06 Å longer.

Analysis of the C-N bond lengths of the central CN₃ core of the guanidine confirm that it is the imine nitrogens which coordinate to the metal as these distances significantly shorter than for the non-ligating nitrogens [1.312(8) and 1.295(8) Å c.f. range 1.342(8) - 1.384(8) Å]. Further to this the NH hydrogens were located in Fourier-difference maps and their attachment to the non-ligating nitrogen also indicates that it is the imine nitrogens that are involved in coordination.
3.3.3 ATTEMPTED FORMATION OF $[\text{Co}_2\{\mu - \eta^2-(N\text{Ph})_2\text{CPh}\}_4]$  

The reaction of 33 with a strong base expected to follow the mechanism shown (Fig. 3.5).

\[
\text{Cl}^- \quad \text{Co}^+ \quad \text{NHR} \quad \text{NHR} \quad + 4 \text{MeLi} \quad \text{THF} \quad \text{Co}^+ \quad \text{NHR} \quad \text{NHR} \quad - 4 \text{MeH} \quad \text{Cl}^- \\
\]

\[2 \text{Cl}^- \quad \text{Co}^+ \quad \text{NHR} \quad \text{NHR} \quad + 4 \text{LiCl} \quad \text{RHN} \quad \text{RHN} \quad - 4 \text{LiCl} \]

*Figure 3.5. Mechanism for dimer formation.*

Treatment of 33 with MeLi evolved a gas and the solution turned dark green. The solution was found to be extremely air-sensitive, contact with air causing the solution to turn brown. Attempts to isolate a product directly from the green solution and from the oxidised material failed.

Exposure of the solution to air caused the solution to turn brown in colour from which a brown solid was precipitated. In order to promote the crystallinity of this solid, attempts were made to exchange the counterion (presumed to be superoxide) with the bulkier PF$_6^-$ and BPh$_4^-$ anions in acetonitrile solution. Unfortunately it also proved impossible to crystallise the brown products obtained from these exchange reactions.

Although it was not possible to cleanly isolate any product from these reactions and so no meaningful analysis was obtained, it is clear that a reaction has occurred. If this product is indeed the expected dimer, its air-sensitivity is of marked difference to $[\text{Co}_2\{\mu - \eta^2-(N\text{Ph})_2\text{CPh}\}_4]$, the corresponding amidinate complex which is air stable. Indeed the air-sensitivity of the resultant green solution may indicate that the dimer has formed, its ready oxidation arising from the ability of the guanidinate ligands to stabilise higher oxidation states (see page 26). Similar behaviour was observed in the $[\text{Mo}_2\{\mu - \eta^2-(N\text{Ph})_2\text{CNHPh}\}_4]^{0+2-}$ system, which was also air-sensitive (undergoing a one-electron oxidation at -0.05 V), while the amidinate analogue was air stable. (3-20)
3.4 EXPERIMENTAL

Solvents were distilled from sodium / benzophenone (THF), sodium (toluene) and P₂O₅ (acetonitrile) under nitrogen. Schlenk-type glassware was used for all reactions though products were handled in air and untreated solvents.

Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FTIR spectrometer. Elemental Analysis was determined using a Perkin Elmer 2400 CHN Elemental Analyser. (+ve FAB) Mass spectra were obtained using a Kratos MS50TC spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Nuclear Magnetic Resonance spectra were recorded on Bruker AC200 and Bruker AC250 spectrometers with positive chemical shifts referenced to TMS. UV/VIS were recorded on a Unicam UV2-100 Series spectrometer.

Silver(I) salts are light sensitive so care was taken to exclude light from the reaction mixtures and products. AgSO₃CF₃ was used as received (Aldrich) while AgBPh₄ was prepared from AgNO₃ and NaBPh₄ in water. CoCl₂ (Aldrich) was dried by heating to reflux in an excess of thionyl chloride for 30 mins. followed by drying at 50°C under dynamic vacuum for one hour.

3.4.1 REACTIONS WITH SILVER(I) SALTS

REACTION OF SILVER(I) TRIFLATE IN ACETONITRILE

In the absence of light, silver(I) triflate (348 mg, 1.06 mmol) was dissolved in acetonitrile (3 cm³) forming a palely coloured solution. To this, triphenylguanidine (696 mg, 2.11 mmol, 2 eq.) was added with acetonitrile (2 cm³) forming a brown solution immediately. After stirring for two hours, ether (30 cm³) was added precipitating a cream coloured solid. This was isolated by filtration, then redissolved in acetonitrile (5 cm³) and layered with ether (20 cm³). However, no crystalline material was obtained, a very fine powder being all that was produced.
REACTIONS OF SILVER(I) TRIFLATE IN TOLUENE

These reactions follow the general procedure outlined by Cotton, et al.\(^{1-6}\)

In the strict absence of light, silver(I) triflate with two molar equivalents of substituted guanidine were weighed into a Schlenk under nitrogen which was then evacuated for 30 mins. to remove any residual moisture. Toluene was added, dissolving most of the solid, then the mixture was refluxed under an inert atmosphere for one hour. Details of isolation, crystallisation and analytical details pertinent to each reaction will be recounted individually.

\[ \text{SYNTHESIS OF } [\text{Ag} \{\text{PhN} = \text{C(NHPh)}\}_2] \left[ \text{SO}_3 \text{CF}_3 \right] \quad 31. \]

Silver(I) triflate (427 mg, 1.66 mmol)
Triphenylguanidine (955 mg, 3.32 mmol)
Toluene (40 cm\(^3\))

After cooling to room temp. the mixture was filtered through a Celite pad to remove a brown precipitate and the resulting pale pink solution was dried \textit{in vacuo}. The pale pink solid obtained was dissolved in the minimum volume of toluene (10 cm\(^3\)) and this was carefully layered with hexane (30 cm\(^3\)). After two days at room temp. colourless crystals suitable for X-ray crystallography were obtained (720 mg, 52\%). CHN: C\(_{39}\)H\(_{34}\)AgF\(_3\)N\(_6\)O\(_3\)S requires C 56.32, H 4.12, N 10.11; Found C 57.67, H 4.51, N 10.54; \textbf{IR} (nujol mull): \(\nu_{\text{max}}\) 3366 (m) (N-H), 3304 (m) (N-H), 1618 (s) (C=N) and 1032 (s) (C-F) cm\(^{-1}\); \textbf{MS} (+ve FAB): \(m/z\) 684 [M+H\(^+\)], 394 [M\(^+\)-triphenylguanidine], 288 [triphenylguanidine] and 194 [diphenylcarbodiimide]; \textbf{\(^1\)H NMR} (250 MHz, CDC\(_3\)): \(\delta\) 6.92-7.17 (m, 15H, ArH), 7.37 (br, 2H, NH) ppm; \textbf{\(^{13}\)C NMR} (62.9 MHz, CDC\(_3\)): \(\delta\) 122.8, 124.6, 129.1 (ArC), 152.7 (quatC) ppm.

\textbf{Crystal Data for 31.}

Data were collected using Mo-K\(\alpha\) radiation in the range 5\(\leq\)2\(\theta\)\(\leq\)45\(^\circ\) on a Stoe Stadi4 diffractometer equipped with an Oxford Cryosystems low temperature device\(^{3-21}\) using \(\omega-\theta\) scans. Owing to rather low crystal quality, characterised by poor peak shapes and backgrounds, a consistent set of \(\psi\) scans could not be obtained, leaving little option but to apply a correction during refinement (DIFABS, correction
applied to $F_c$ maximum and minimum corrections 1.347 and 0.683, respectively). The structure was solved by direct methods (SIR 92).\textsuperscript{(3,22)} 31 was refined against $F$ using 2895 data with $F > 4\sigma(F)$ (out of a total of 4264 unique data, CRYS
tALS).\textsuperscript{(3,24)} Hydrogen atoms were placed in calculated positions and anisotropic displacement parameters were refined for all other atoms, giving a final $R$ of 0.0639, $R' = 0.0704$ for 481 parameters. The final difference-map extrema were 0.81 and -1.32 e Å$^{-3}$.

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*Table 3.4. Crystallographic Data for 31.*

**SYNTHESIS OF [Ag(BuN=GNfI 1Bu))$_2$][SO$_3$CF$_3$] 32.**

Silver triflate (348 mg, 1.35 mmol)
Tri-(tert-butyl)guanidine (616 mg, 2.71 mmol)
Toluene (30 cm$^3$)

While refluxing a silver mirror was deposited on the wall of the Schlenk and after cooling, filtration through celite yielded a colourless solution. The solvent was removed *in vacuo* leaving an off-white solid and a colourless oil. The infrared spectrum of this mixture showed a strong peak at 1650 cm$^{-1}$ [$\nu$(C=N) in the free ligand] though this had a shoulder at 1600 cm$^{-1}$ [$\nu$(C=N) in the bound ligand]. The oil was removed by washing with hexane (2 x 20 cm$^3$) and after drying, the hexane washings yielded a colourless oil [$\nu$(C=N) 1650 cm$^{-1}$]. The residual cream coloured solid was collected by filtration and dried *in vacuo* for two hours (230 mg, 24%); CHN C$_{27}$H$_{58}$AgF$_3$N$_6$O$_3$S requires C 45.56, H 8.21, N 11.81; Found C 44.41, H 8.14,
N 11.02; IR (nujol mull): $\nu_{\text{max}}$ 3341 (br, m) (N-H), 1605 (s) (C=N) and 1032 (s) (C-F) cm$^{-1}$; MS (+ve FAB) : $m/z$ 228 [tri-(tert-butyl)guanidine] and 154 [di-(tert-butyl)carbodiimide]; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 1.41 (s, 27H, C(CH$_3$)$_3$), 5.16 (br, 2H, NH) ppm; $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$ 29.8 (CH$_3$), 53.4 (CMe$_3$), 120.5 (q, $J = 320$ Hz, CF$_3$), 152.4 (quatC) ppm.

**Attempted Synthesis of [Ag(CyxN=C(NH(Cyx))$_2$][SO$_3$CF$_3$]**

Silver(I) triflate (389 mg, 1.51 mmol)
Tricyclohexylguanidine (925 mg, 3.03 mmol)
Toluene (40 cm$^3$)

The silver triflate and guanidine were combined in a darkened flask and dried. Toluene was added and the mixture was stirred for twenty-four hours at room temp. Solution infrared spectra in toluene recorded at hourly intervals for the first three hours showed no change in the $\nu$(C=N) band of the guanidine. The mixture was left stirring for twenty-four hours though no change was observed in the infrared spectrum indicating no reaction had occurred. No further analysis of the reaction mixture was undertaken.

**Attempted Synthesis of [Ag({\alpha-MeBz})N=C(NH{\alpha-MeBz})$_2$][SO$_3$CF$_3$]**

Silver(I) triflate (209 mg, 0.82 mmol)
Tris((s)-(-)-\alpha–methylbenzyl)guanidine (604 mg, 1.63 mmol)
Toluene (40 cm$^3$)

This reaction was attempted in a similar manner to the previous guanidines in that the reaction mixture was heated to reflux temperature for one hour. While refluxing, a silver mirror deposited on the walls of the Schlenk. After cooling the reaction mixture was filtered through a Celite pad to remove a dark solid, producing a pale yellow solution from which a yellow oil was obtained. This was dissolved in toluene (10 cm$^3$) and storage of this solution at room temp., 5°C and -30°C only produced precipitate. Attempts to crystallise the oil from a toluene solution layered with hexane also failed. No analysis of this oil was undertaken.
**REACTION OF SILVER(I) TETRAPHENYLBORATE IN ACETONITRILE**

Following a similar procedure to the reaction carried out in toluene, silver tetrphenylborate (120 mg, 0.28 mmol) and tris((s)-(−)-α-methylbenzyl)guanidine (209 mg, 0.56 mmol) were combined in a darkened flask and dried. Acetonitrile (30 cm³) was added and the mixture was heated to reflux, under nitrogen, for one hour. After cooling the mixture was filtered through Celite, removing a large quantity of black solid, yielding a colourless filtrate. Volatiles were removed from the filtrate *in vacuo* though no product material was recovered. Therefore, the only product obtained from the reaction was the black solid which proved insoluble in organic solvents. No analysis of this product was undertaken.

### 3.4.2 REACTIONS OF COBALT(II) CHLORIDE

The general reaction scheme employed in these reactions was first outlined by Cotton, *et al.*<sup>(3-5)</sup> Only triphenylguanidine was studied in these reactions and all reactions were performed in solution, *i.e.* solvent free melt reactions were not attempted.

**ATTEMPTED SYNTHESIS OF [Co{PhN=C(NHPh)₂}₂Cl₂] IN TOLUENE.**

Following the method of Cotton *et al.*,<sup>(3-5)</sup> anhydrous CoCl₂ (196 mg, 1.51 mmol), triphenylguanidine (512 mg, 1.78 mmol) and dry toluene (20 cm³) were combined in a flask and refluxed, under a nitrogen atmosphere, for twenty-four hours. Initially the solution was a very pale blue colour though in time the solution turned progressively deeper and ultimately became bright blue in colour. Hot filtration removed a small amount of a blue precipitate. Upon cooling to room temperature the solution lost much of its intense colour and pink, unreacted CoCl₂ precipitated. It was obvious from the quantity of CoCl₂ recovered that very little had actually reacted.
SYNTHESIS OF \([\text{Co}\{\text{PhN} = \text{C(NHPh)}_2\}_2\text{Cl}_2]\) IN THF 33.

Anhydrous CoCl$_2$ (0.42 g, 3.20 mmol), triphenylguanidine (1.84 g, 6.40 mmol) and dry THF (20 cm$^3$) were combined in a flask and refluxed, under an nitrogen atmosphere, for twenty-four hours. Upon addition of the THF a bright blue solution formed which remained unchanged through the course of the reaction. The bright blue solid obtained after the solvent was removed in vacuo was dissolved in CH$_2$Cl$_2$ (50 cm$^3$) and the solution filtered through a pad of Celite. Hexane was added until precipitation commenced and the precipitate was redissolved by adding CH$_2$Cl$_2$ dropwise. Crystallisation by slow evaporation yielded blue and colourless crystals (complex and unreacted ligand). The blue crystals were recrystallised from CH$_2$Cl$_2$ and a small amount of well formed needles of 33 were obtained which were suitable for X-ray diffraction.

The yield of these crystals was insufficient for analysis so the reaction was repeated on a larger scale; CoCl$_2$ (1.85 g, 12.27 mmol), triphenylguanidine (8.20 g, 28.53 mmol) and dry THF (90 cm$^3$). Also, in an attempt to increase the yield, the reaction mixture was maintained at reflux temperature for 89 hours. Crystallisation from CH$_2$Cl$_2$ and hexane again yielded blue needles of 33·2CH$_2$Cl$_2$ (8.20 g, 77%); CHN : C$_{40}$H$_{38}$Cl$_6$CoN$_6$ requires C 54.92, H 4.35, N 9.61; Found C 63.61, H 4.75, N 11.82. This is consistent with solvent loss by the crystals of approximately 1.8 molecules of CH$_2$Cl$_2$ per molecule of 33. 33·0.2CH$_2$Cl$_2$ requires C 63.58, H 4.77, N 11.65). IR (nujol mull): $\nu_{\text{max}}$ 3351 (m) (N-H) and 1626 (m) (C=N) cm$^{-1}$; MS (+ve FAB): $m/z$ 704 [M+H$^+$], 668 [M-Cl], 633 [M-2Cl], 612 [M-NHPh] and 288 [triphenylguanidine]; UV/VIS (CH$_2$Cl$_2$): $\nu$/cm$^{-1}$ = 40 000 ($\varepsilon = 24 550$) and 15 360 ($\varepsilon = 345$ dm$^3$ mol$^{-1}$ cm$^{-1}$).

Crystal Data for 33.

Data were collected using Mo-K$_\alpha$ radiation in the range $5 \leq 2\theta \leq 50^\circ$ on a Stoe Stadi4 diffractometer equipped with an Oxford Cryosystems low temperature device$^{(3-21)}$ using $\omega-\theta$ scans. An absorption correction based on $\psi$ scans was applied (maximum and minimum transmission coefficients: 0.540 and 0.498), $R_{\text{int}} = 0.1958$ (based principally on a weak high-angle data). The structure was solved by direct
methods (SIR 92)\(^{(3-23)}\). \(33\) was refined against \(F^2\) (SHELXTL)\(^{(3-25)}\) with anisotropic displacement parameters for all non-H atoms, and H atoms placed in calculated positions, although those attached to nitrogen were discernible in a difference map. The refinement converged to \(R_1 = 0.0759\) [based on \(F\) and 7721 data with \(F > 4\sigma(F)\)] and \(wR_2 = 0.2013\) [based on \(F^2\) and all 14784 data] for 956 parameters. The final difference-synthesis maximum and minimum were +0.51 and -0.50 e Å\(^3\), respectively.

---

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**Table 3.5. Crystallographic Data for 33.**

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**ATTEMPTED SYNTHESIS OF \([\text{Co}_2\{\mu - \eta^2-(\text{NPh})_2\text{CNHPh}\}_2]\)**

\([\text{Co}\{\text{PhN}=(\text{NHPh})_2\}_2\text{Cl}_2\cdot2\text{CH}_2\text{Cl}_2\, (5.01\,\text{g}, \,5.73\,\text{mmol})\) was completely dissolved in THF (20 cm\(^3\)) in order to release the \(\text{CH}_2\text{Cl}_2\) from the crystals, then the solvent was removed to dryness. The resultant blue powder was redissolved in THF (20 cm\(^3\)) and the solution cooled to -78°C. Addition of MeLi (7.8 cm\(^3\) of a 1.6 mol dm\(^{-3}\) solution in ether, 12.5 mmol) caused the immediate formation of a green solution with evolution of an unidentified gas. The solution was warmed to room temp. during which time the solution darkened in colour. The solvent was removed in vacuo and the residual solid dissolved in ether (30 cm\(^3\)). Filtration removed LiCl to leave a clear green solution. Attempts to crystallise this product directly failed.
Following exposure of this solution to air a brown precipitate was obtained. Attempts to crystallise this by exchange of the counterions failed and no analysis was obtained on the brown solid.
3.5 REFERENCES

CHAPTER FOUR

REACTIONS WITH RUTHENIUM HALF-SANDWICH COMPLEXES

4.1 INTRODUCTION

Reactions of guanidines with ruthenium half-sandwich complexes formed the early part of my PhD work. The work undertaken was based on the reaction of ruthenium cyclopentadienyl (RuCp), ruthenium pentamethycyclopentadienyl (RuCp*) and ruthenium arene complexes with tri-substituted guanidines. These ruthenium complexes were attractive as starting materials for a number of reasons:

- Their synthesis was well known and readily achievable.\(^{4,1,4,2,4-3,4,4}\)
- Their mild air- and moisture sensitivity allowed experience to be gained in working with organometallic complexes.
- They allowed access to a metal centre in a variety of coordination modes and oxidation states.
- Reaction of these complexes with nitrogen donor ligands was known.\(^{4-5,4-6}\)
- Previous work with guanidines and ruthenium arene complexes had proved successful.\(^{4-7}\)

The reaction of these complexes with guanidines will be discussed, as will details of their synthesis.

4.2 REACTIONS WITH RUTHENIUM CYCLOPENTADIENYL COMPLEXES

The first series of ruthenium complexes that the guanidine ligands could be reacted with were \(\eta^5\)-cyclopentadienyl ruthenium carbonyl complexes, synthesised from triruthenium dodecacarbonyl, \([\text{Ru}_3(\text{CO})_{12}]\) (Fig. 4.1).\(^{4-1}\) The first starting material of interest was the cationic species acetonitriledicarbonyl(\(\eta^5\)-
cyclopentadienyl)ruthenium(II), $[\text{Ru} \text{Cp} \text{(CO)}_2 \text{(NCMe)}]^+$, which was expected to be obtainable from tetracarbonylbis($\eta^5$-cyclopentadienyl)diruthenium, $[\text{Ru}_2 \text{Cp}_2 \text{(CO)}_4]$. Further reaction of this would give diacetonitrilemonocarbonyl($\eta^5$-cyclopentadienyl)ruthenium (II), $[\text{Ru} \text{Cp} \text{(CO)} \text{(NCMe)}_2]^+$, which would be of interest as the acetonitrile ligands are only very weakly coordinated and hence are very labile. This would lead to the guanidine chelating to the ruthenium and with subsequent loss of a CO ligand it would be possible to coordinate the guanidine in the $\eta^4$ mode.

![Figure 4.1. Formation of Ruthenium Cyclopentadienyl carbonyl complexes](image)

Triruthenium dodecacarbonyl, $[\text{Ru}_3 \text{(CO)}_{12}]$, was converted into tetracarbonylbis($\eta^5$-cyclopentadienyl)diruthenium, $[\text{Ru}_2 \text{Cp}_2 \text{(CO)}_4]$, by refluxing in heptane in the presence of cyclopentadiene. This was first performed under dinitrogen to form the intermediate hydride, $[\text{Ru} \text{Cp} \text{(CO)}_2 \text{H}]$, then in air to yield the dimer, $[\text{Ru}_2 \text{Cp}_2 \text{(CO)}_4]$, which formed orange crystals on cooling to room temperature. The product showed four bands in the carbonyl region of the IR spectrum and only one peak in the $^1\text{H}$ NMR spectrum, as anticipated, due to Cp hydrogens. However, the $^{13}\text{C}$ NMR spectrum showed only two peaks, one corresponding to the Cp carbons and one for the CO ligands. Only one peak is observed for the CO’s due to the fluxional nature of the compound, around the Ru-Ru bond, which averages the terminal and bridging carbonyls. The product was
found to be light and air sensitive, particularly in solution, forming an insoluble brown material on standing.

This product, \([\text{Ru}_2\text{Cp}_2(\text{CO})_4]\), was subsequently used to synthesise acetonitriledicarbonyl(\(\eta^5\)-cyclopentadienyl)ruthenium (II) tetrafluoroborate, \([\text{RuCp(}CO)_2(\text{NCMe})]\text{BF}_4\), by oxidation with silver tetrafluoroborate in a dichloromethane / acetonitrile mixture. The reaction was successful (IR bands at 2079, 2032 cm\(^{-1}\))\(^{(4-9)}\) and colourless crystals of the product were isolated and characterised. However, the product was only obtained in a very poor yield which meant that it was not feasible to make an attempt at the subsequent reactions. Formation of the BF\(_4\) salt was also attempted in the dark to prevent oxidation of the \([\text{Ru}_2\text{Cp}_2(\text{CO})_4]\) before it reacted although the IR spectrum showed that there were still impurities in the product after isolation, hence purification was still required as before.

The analogous reaction to form \([\text{RuCp(}CO)_2(\text{NCMe})]\text{SO}_3\text{CF}_3\) was also attempted using silver triflate as the oxidising agent. The \([\text{Ru}_2\text{Cp}_2(\text{CO})_4]\) starting material was washed through a pad of alumina to purify it immediately before reaction. The reaction was successful in that \([\text{RuCp(}CO)_2(\text{NCMe})]\text{BF}_4\) was formed (IR bands at 2081, 2034 cm\(^{-1}\))\(^{(49)}\) but an impurity was still present (2001 cm\(^{-1}\)) which was thought to be caused by the triflate anion coordinating directly to the ruthenium by displacement of the acetonitrile ligand.

Due to the problems arising in the synthesis of the ruthenium cyclopentadienyl carbonyl complexes it was decided to use some known pentamethylcyclopentadienyl ruthenium complexes as starting materials to react with guanidine ligands.

### 4.3 REACTIONS WITH RUTHENIUM PENTAMETHYL CYCLOPENTADIENYL COMPLEXES

Prior to synthesising the ruthenium pentamethylcyclopentadienyl complexes, it was required to have a source of pentamethylcyclopentadiene. Although pentamethylcyclopentadiene is commercially available it is very expensive and the most economically viable option was to prepare a large amount of the ligand.
A number of methods for the synthesis had been reported although the method followed appeared to be the most straightforward.

4.3.1 Large Scale Synthesis of Pentamethylcyclopentadiene

Pentamethylcyclopentadiene \((\text{Cp}^*, \text{C}_5\text{Me}_5)\), was synthesised in the following three step process (Fig. 4.2).

![Figure 4.2. Synthetic Route to Pentamethylcyclopentadiene.](image)

The first step is the formation of 2,3,5,6-tetrahydro-2,3,5,6-tetramethyl-\(\gamma\)-pyrone which is achieved by deprotonation at the \(\beta\) carbons of 3-pentanone followed by addition of a mole of acetaldehyde onto each \(\beta\) carbon. Ring closure via the loss of water then follows to yield the product. Analysis of the IR spectrum shows two peaks in the carbonyl region:- 1712 cm\(^{-1}\) from the product and a smaller peak at 1674 cm\(^{-1}\) from the intermediate \(\alpha,\beta\)-unsaturated ketone.\(^{4-10}\) Evidence for this is also found in the \(^1\)H NMR spectrum but the product was not further purified as the intermediate does not affect the subsequent reaction.

The second step forms 2,3,4,5-tetramethylcyclopent-2-enone, the mechanism being a double acylation followed by dehydration. The formic and sulphuric acids combine to form an acid anhydride which performs the acylations. The IR spectrum shows characteristic frequencies for \(\alpha,\beta\)-unsaturated 5 membered ring ketones: \(^{4-11}\) 1670, 1651 cm\(^{-1}\) and the \(^1\)H NMR spectrum is also consistent with the desired product.

The final step in the synthesis forms 1,2,3,4,5-pentamethylcyclopentadiene. This is achieved by the alkylation of the \(\alpha\) carbon by methyl lithium followed by dehydration to yield the diene. Spectroscopic analysis of the resulting pale yellow liquid proved that the synthesis had been successful producing \(\text{Cp}^*\) in a yield of 62\%.
Following the preparation of Cp*, the next stage was the synthesis of the ruthenium pentamethylcyclopentadienyl starting complexes.

4.3.2 **Ruthenium Pentamethylcyclopentadienyl Complexes**

The series of RuCp* complexes which were synthesised were based on the reactions initially reported by P.J. Fagan, *et al.*,\(^{(4-3)}\) from the starting material di-\( \mu \)-chloro-bis(\( \eta^5 \)-pentamethylcyclopentadienyl)chlororuthenium (III), [Cp*RuCl\(_2\)]\(_2\) (Fig. 4.3). This was prepared from ruthenium trichloride with pentamethylcyclopentadiene in refluxing methanol\(^{(4-2)}\) and characterised by IR and \(^1\)H NMR spectroscopy. Reduction of this with lithium triethylborohydride in THF produced the tetrameric complex tetra-\( \mu \)-chloro-tetrakis(\( \eta^5 \)-pentamethylcyclopentadienyl)ruthenium (II), [RuCp*Cl]\(_4\), which assumes a tetranuclear cubane like structure, and was characterised by elemental analysis and \(^1\)H NMR spectroscopy. This can subsequently be reacted to form trisacetonitrile(\( \eta^5 \)-pentamethylcyclopentadienyl)ruthenium (II) triflate, [Cp*Ru(NCMe)\(_3\)]SO\(_3\)CF\(_3\), by the action of silver triflate in refluxing acetonitrile.\(^{(4-12)}\)

\[
\begin{align*}
\text{RuCl}_3 + \text{Cp}^*\text{H} & \rightarrow \quad \text{RuCp}^* \\
\text{NCMe} & \text{NCMe} \\
\text{NCMe} & \text{NCMe}
\end{align*}
\]

*Figure 4.3. Synthesis of RuCp* Complexes.*
4.3.3 **REACTIONS OF RuCp* WITH GUANIDINES**

4.3.3.1 **REACTIONS OF [Cp*RuCl₂]₂**

[Cp*RuCl₂]₂ was known to undergo cleavage reactions with neutral two electron donor ligands (L) to form complexes of the type [Cp*RuCl₂L].(45) However, as guanidines have the possibility to undergo deprotonation reaction was expected to result in the formation of complexes containing monoanionic chelating guanidinate ligands, *i.e.* [Cp*RuCl(L-L)] where L-L signifies a chelating guanidinate ligand.

This is analogous to the reaction of guanidines with [{Ru(η-MeC₆H₄Pr-p)Cl₂}]₂, the major difference being the oxidation state of the metal. With the arene ligand ruthenium is in oxidation state II, while with the anionic Cp* it is in oxidation state III.

This reaction requires two equivalents of guanidine per metal, the first equivalent being deprotonated while the second is protonated and forms the hydrogen chloride salt. This can be represented by the following reaction (Fig. 4.4).

![Figure 4.4. Formation of deprotonated and protonated guanidine ions.](image)

Reactions of this type were undertaken with treatment of [Cp*RuCl₂]₂ with two molar equivalents of tri-p-tolylguanidine. The reactions were performed in toluene, [Cp*RuCl₂]₂ being soluble enough in toluene to react with the guanidine. Upon addition of the guanidine to the suspension, an immediate colour change was observed from dark brown of [Cp*RuCl₂]₂ to a deep green. With stirring at room temperature, the reaction solution turned orange and a pale coloured precipitate formed. Filtration of this gave a clear orange precipitate from which purification and isolation of a product was attempted.

As the ruthenium remained in oxidation state III the metal was paramagnetic which hampered NMR study of the reaction product(s). Crystallisation of a product directly from the reaction mixture was attempted by a variety of means; from toluene solution and also from DCM / hexane mixtures. As no crystalline products were
obtained, purification was attempted by thin layer and column chromatography although the products were not robust enough and decomposed in the presence of silica and alumina.

Therefore, with NMR study being of little value and single crystals proving elusive, no structural data was obtained for these products.

4.3.3.2 REACTIONS OF \([\text{Cp}^*\text{RuCl}]_4\)

\([\text{Cp}^*\text{RuCl}]_4\) is a very interesting material which forms a tetrameric cube in the solid state.\(^{(4-3)}\) However, it is soluble in coordinating solvents in which the cube disassembles to form discrete monomeric units. For this reason \([\text{Cp}^*\text{RuCl}]_4\) may be viewed as an electron deficient species which will readily undergo substitution. In fact, neutral bidentate ligands, \(\text{e.g.}\) 2,2'-bipyridine, were known to readily coordinate to \([\text{Cp}^*\text{RuCl}]_4\) forming complexes of the type \([\text{Cp}^*\text{RuClL}_2]\) (where \(L_2\) is a bidentate ligand).\(^{(4-13)}\)

As attractive a starting material as \([\text{Cp}^*\text{RuCl}]_4\) seems it is not ideal for reaction with guanidines. With the ruthenium centre being in oxidation state II, reaction with anionic ligands would result in an ionic products and it would be unlikely for the guanidine to chelate the metal centre without undergoing a deprotonation. Nonetheless, reactions with tri-\(p\)-tolyguanidine were attempted, and where an excess of guanidine was used, an additional neutral donor molecule was added in an attempt to replace the chloride ligand removed as the guanidine HCl salt.

The reactions were carried out in two different stoichiometries, one equivalent of guanidine per Ru and two equivalents per Ru. In the 1:1 reaction, addition of the guanidine to \([\text{Cp}^*\text{RuCl}]_4\) in THF solution, resulted in the formation of a green solution and a pale precipitate. The precipitate was isolated and found to equal the weight expected of four equivalents of the guanidine HCl salt. Hence it appeared that no guanidine remained in the reaction mixture.

The reaction of eight equivalents of guanidine with \([\text{Cp}^*\text{RuCl}]_4\) proceeded as for the previous reaction, the solution turning green in colour and a white
precipitate being produced. The precipitate was isolated and was equal in weight to four equivalents of the guanidine HCl salt. Attempts were made to crystallise a product directly from the filtrate and also after the addition of four equivalents of PPh₃ though all these attempts failed to yield a product. Chromatography was also attempted though this also failed as decomposition occurred before any product could be eluted from the column.

Even with the metal centre being diamagnetic, it was not possible to collect meaningful NMR spectra of the reaction mixtures as it appeared a variety of products existed in solution. This is also due in part to the magnetically active nuclei being removed from the sites of coordination and so if a difference was detected from the NMR spectrum, it was difficult to interpret this without full structural information.

4.3.3.3 REACTIONS OF \([\text{Cp}^*\text{Ru(NCMe)}_3]^+\)

\([\text{Cp}^*\text{Ru(NCMe)}_3]^+\) was also an interesting starting material to consider as it has an interesting reactivity, in that while the acetonitrile ligands are labile as expected, the \([\text{Cp}^*\text{Ru}]^+\) fragment is known to favour \(\eta^6\) aromatic ligands.\(^{(4-12)}\) This happens to such an extent that if \([\text{Cp}^*\text{Ru(NCMe)}_3]^+\) is dissolved in THF dried over benzophenone, then the complex isolated will be \([\text{Cp}^*\text{Ru(}\eta^6\text{-benzene})]\) even if there is no other source of benzene present other than from the benzophenone.\(^{(4-12)}\) Care had to be taken therefore, to exclude aromatic groups from the reaction mixture, except in the cases where tri-\(p\)-tolylguanidine was reacted with \([\text{Cp}^*\text{Ru(NCMe)}_3]^+\) to produce such a complex.

Indeed, these were the first reactions to be attempted with this starting material. Tri-\(p\)-tolylguanidine was treated with \([\text{Cp}^*\text{Ru(NCMe)}_3]^+\) in the ratios 1:1, 1:2 and 1:3, the anticipated product being tri-\(p\)-tolylguanidine with one, two and three \([\text{Cp}^*\text{Ru}]^+\) fragments bound onto the \(p\)-tolyl groups. The reactions were carried out in refluxing THF solution and following cooling to room temperature and filtration, the addition of ether precipitated a white solid. Attempts were made to crystallise the solid from THF / ether mixtures and although the 2:1 and 3:1 reactions did not yield any crystals, the 1:1 reaction yielded a crop of colourless crystals 41. The crystals were suitable for X-ray diffraction and the molecular structure was determined (Fig. 4.6).
Figure 4.6. Molecular structure of 41. Triflate anion omitted for clarity.


The complex $\left[\eta^5-Cp^*\right]Ru(\eta^6-p$-tolyl)NC(HN-p-tolyl)$_2][\text{SO}_3\text{CF}_3]$ was found to have the structure anticipated. The guanidine is bound $\eta^6$ to the ruthenium centre through one of its $p$-tolyl groups. The crystal structure confirms that the $p$-tolyl group is bound to the imine nitrogen of the guanidine [C(1)-N(1) 1.292(8) Å] and also that the guanidine remains as a neutral ligand (hydrogens on N(2) and N(3) located in crystal structure). As for the Silver(I) complex described in Chapter 3, the triflate anion hydrogen bonds to the N-H protons, although the triflate is not shown in this picture.

Spectroscopic data were also obtained for the complex. The $^1H$ NMR shows a broad singlet for the Cp* hydrogens and also broad signals for the uncoordinated phenyl hydrogens. Of more interest was the signals for the coordinated phenyl hydrogens which had shifted from 7.1 to 5.2 ppm. The $^{13}C$ NMR signals for the coordinated phenyl ring had similarly shifted from ca. 130 to 90 ppm. Satisfactory elemental analysis was obtained and FAB mass spec contained a peak at m/z 566 corresponding to the parent cation.

**REACTIONS WITH TRIALKYLGUANIDINES**

Reactions of $[\text{Cp}^*\text{Ru(NCMe)}_3]^+$ with trialkylguanidines were also attempted however these were particularly undistinguished in that the only products isolated from the reactions were the triflate salts of the guanidines.
4.4 REACTIONS WITH RUTHENIUM ARENE COMPLEXES

The ruthenium arene complex used in these reactions was \([\{\text{Ru}(\eta^\text{-MeC}_6\text{H}_4\text{Pr-p})\text{Cl}\}_2\}\], a chloro-bridged dimer formed in the reaction of RuCl_3 with \(\alpha\)-pinene in ethanol.\(^{\text{4-4}}\) The dimer was known to cleave readily upon addition of a donor molecule and the cleavage reaction between triphenylguanidine and \([\{\text{Ru}(\eta^\text{-MeC}_6\text{H}_4\text{Pr-p})\text{Cl}\}_2\}\] was already known prior to my commencing my work in Edinburgh (Fig. 4.7).\(^{\text{4-7}}\)

\[
\text{NR} \quad [\text{Ru}(p\text{-cymene})\text{Cl}]_2 + 4 \text{RHN}\quad \text{toluene} \quad R = \text{Ph}
\]

\[
\begin{align*}
\text{Ru} & \quad \text{Cl} \\
\text{iPr} & \quad \text{Me} \\
\text{N} & \quad \text{R} \\
\text{N} & \quad \text{C} \\
\text{R} & \quad \text{H} \\
\text{N} & \quad \text{R} \\
\text{R} & \quad \text{N} \\
\text{N} & \quad \text{H} \\
\text{R} & \quad \text{N} \\
\text{R} & \quad \text{N} \\
\text{Cl} & \quad \text{N} \\
\text{N} & \quad \text{R} \\
\text{N} & \quad \text{R}
\end{align*}
\]

*Figure 4.7. Synthesis of \([\text{Ru}(\eta^\text{-MeC}_6\text{H}_4\text{Pr-p})\text{Cl}]_2(\eta^\text{2-}(\text{Ph})_2\text{CNPh})\text{Cl})\]*

However, this reaction had not been attempted with any of the other guanidines that were available. Reactions of \([\{\text{Ru}(\eta^\text{-MeC}_6\text{H}_4\text{Pr-p})\text{Cl}\}_2\}\] with different trisubstituted guanidines were attempted by myself with the help of Marie Elliot in her Honours research project. The complex that we were most interested in pursuing was one containing the chiral guanidine, tris((s)-(\(-\)\(-\alpha\)-methylbenzyl))guanidine, although reactions with other ligands were tried.

4.4.1 REACTION WITH TRICYCLOHEXYLGUANIDINE

The first reaction to be attempted was that of tricyclohexylguanidine with the dimer. This was expected to react similarly to the triphenyl ligand, the alkyl substituents not expected to greatly alter the reactivity of the guanidine. Indeed,
treatment of the dimer with four equivalents of the guanidine in toluene solution led to the formation of an orange solution with the formation of a white precipitate. An IR spectrum of the orange solution showed no band at 1650 cm$^{-1}$ from the imine nitrogen which indicates that the guanidine had reacted. The reaction mixture was filtered to remove the precipitate (assumed to be the guanidine salt) to leave a bright orange solution. The solvent was removed to leave a bright orange solid. Attempts were made to crystallise this solid from dichloromethane / hexane mixtures but these failed. No further spectroscopic data was obtained for this product.

The reaction was repeated with similar results. However, TLC of the orange solution indicated that two products were in solution. Therefore, purification was attempted by column chromatography using first silica, then alumina as the stationary phase. However, with both media the same result was obtained. Upon loading the orange solid onto the column and eluting with hexane an orange band began to move down the column. With continued elution the band slowed and in time started to change colour to green. Once the colour had changed completely the band remained stationary and would not elute off the column even with polar solvents. Hence, purification of the reaction product proved problematic and nothing of sufficient purity for analysis was obtained from these reactions.

**4.4.2 REACTION WITH TRIISOPROPYLGUANIDINE**

The reaction was repeated on a similar scale using triisopropylguanidine instead of the tricyclohexyl derivative. There was expected to be little difference between the donor properties of this and the tricyclohexylguanidine although the smaller $^3$Pr groups may give a product with improved crystallinity.

Reaction proceeded as it had for the tricyclohexylguanidine in that an orange solution with pale precipitate formed after stirring at room temperature. The precipitate was filtered off and the solvent removed to dryness. Dichloromethane was added to dissolve the orange residue and this solution was carefully layered with hexane. Following storage at room temperature large red crystals 42 had formed from the reaction mixture. These were isolated by filtration, analysed and X-ray diffraction data collected. The X-ray crystal structure was determined (Fig. 4.8) and the complex was found to be $[\text{Ru}(\eta^5-\text{MeC}_6\text{H}_4\text{Pr}-p)(\eta^2-(N^3\text{Pr})_2\text{CNH}^3\text{Pr})\text{Cl}]$,  

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Figure 4.8. Molecular Structure of 42. Isopropyl CH₃ groups omitted for clarity.

Table 4.2. Selected bond lengths (Å) and angles (°) for 42.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-N(1)</td>
<td>2.078(2) Å</td>
</tr>
<tr>
<td>Ru(1)-N(2)</td>
<td>2.115(2) Å</td>
</tr>
<tr>
<td>Ru(1)-Cl(1)</td>
<td>2.4293(6) Å</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.318(3) Å</td>
</tr>
<tr>
<td>C(1)-N(2)</td>
<td>1.336(3) Å</td>
</tr>
<tr>
<td>C(1)-N(3)</td>
<td>1.383(3) Å</td>
</tr>
<tr>
<td>N(1)-Ru(1)-N(2)</td>
<td>62.07(7) °</td>
</tr>
<tr>
<td>Ru(1)-N(1)-C(1)</td>
<td>94.78(13) °</td>
</tr>
<tr>
<td>Ru(1)-N(2)-C(1)</td>
<td>92.57(13) °</td>
</tr>
<tr>
<td>N(1)-C(1)-N(3)</td>
<td>126.3(2) °</td>
</tr>
<tr>
<td>N(1)-C(1)-N(3)</td>
<td>124.6(2) °</td>
</tr>
<tr>
<td>N(1)-C(1)-N(3)</td>
<td>126.3(2) °</td>
</tr>
<tr>
<td>N(1)-C(1)-N(3)</td>
<td>124.6(2) °</td>
</tr>
</tbody>
</table>
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analogous to the triphenylguanidinate complex previously characterised. The complex contained a central Ru centre coordinated by a $\eta^6$ p-cymene ligand, a chelating monoanionic guanidinate ligand and a terminal chloride. There is very little difference in the geometry of the trisopropyl ligand versus the triphenyl one and if a slight difference in electronic properties exists, they would likely be too small to be observed from the crystal structure. The chelate bonds are not symmetrical [Ru(1)-N(1) 2.078(2) Å and Ru(1)-N(2) 2.115(2) Å] as was also found in the triphenyl complex [Ru(1)-N(1) 2.087(3) Å and Ru(1)-N(2) 2.103(3) Å]. Another similarity to the triphenyl complex are the bond lengths within the central CN$_3$ core of the guanidine. The bonds to the metal coordinated nitrogens are shorter [C(1)-N(1) 1.318(3) and C(1)-N(2) 1.336(3) Å] than that for the uncoordinated nitrogen [C(1)-N(3) 1.383(3) Å] indicating that the negative charge is delocalised over N(1), C(1) and N(2). The idea of delocalisation over the guanidine is confirmed by inspection of the bond angles around the central CN$_3$ core [N(1)-C(1)-N(2) 109.1(2)°, N(1)-C(1)-N(3) 126.3(2)° and N(2)-C(1)-N(3) 124.6(2)°] which total 360° indicating strict planarity at the heart of the ligand.

Following this successful repeat of the reaction of [{Ru(i-MeC$_6$H$_4$Pr-p)Cl$_2$}]$_2$ with a trisubstituted guanidine, attempts were made to characterise a complex containing the chiral guanidine tris((s)-(-)-(x—methylbenzyl)guanidine.

4.4.3 Reaction with Tris((S)-(−)-(x—Methylbenzyl)guanidine

This reaction was undertaken in the same manner as previous ones. The guanidine and the [{Ru(η-MeC$_6$H$_4$Pr-p)Cl$_2$}]$_2$ were stirred together in toluene. From the initial red colour the solution turned orange and a precipitate formed. To ensure the reaction went to completion the mixture was left stirring under nitrogen for two days. An IR spectrum of the orange solution showed that no band from the imine persisted (1651 cm$^{-1}$ in the free ligand). The mixture was filtered and the toluene was removed to leave a sticky orange oil. The oil was dissolved in dichloromethane and hexane was layered to crystallise. Unfortunately, no crystalline material formed so the solution was dried in vacuo and analysed by TLC. Elution with ethanol caused two distinct spots to move from the baseline – a fast moving orange spot and a slower brown spot. As column chromatography had previously failed on these
complexes, preparation TLC was used to separate the two products in an attempt to reduce the time the complex spends on the silica to a minimum. Again elution caused the two coloured spots to separate although it proved impossible (even with Soxhlet extraction) to recover the products from the silica.

Therefore a pure product was not obtainable from this reaction, either by direct crystallisation or from chromatographic separation. This is no doubt due to a combination of factors;

- The impurity which hampered the crystallisation of tris((s)-(-)-α-methylbenzyl)guanidine has also affected the crystallisation of a product from this reaction. This being the case, it may be necessary to remove this impurity or crystallisation of future reaction products may also be hindered.

- The guanidinate complexes are not stable on silica gel and as another compound persisted in the reaction mixture it proved impossible to crystallise. This was unfortunate as crystallisation is the method of choice for separating air and moisture stable complexes.

That a fully characterised complex containing a chiral guanidine ligand was not obtained was disappointing as such a complex would have been very interesting and could have lead to a study of the catalytic action of guanidinate containing complexes.\(^{(4-14)}\)
4.5 EXPERIMENTAL

All air sensitive reactions were manipulated using Schlenk-type apparatus under an atmosphere of dry, oxygen free nitrogen or under vacuum.\(^{(4-15)}\) All solvents were deoxygenated and dried before use by distillation from sodium / benzophenone for ethers (except for \([\text{Cp}^*\text{Ru} (\text{NCMe})_3]^+\) reactions), \(\text{P}_4\text{O}_{10}\) for acetonitrile and \(\text{CaH}_2\) for hydrocarbons and dichloromethane.

Infrared spectra were recorded on a Perkin Elmer 1600 Series FTIR spectrometer. Elemental Analysis was determined using a Perkin Elmer 2400 CHN Elemental Analyser. \((+/-\text{ FAB})\) Mass spectra were obtained using a Kratos MS50TC spectrometer. Nuclear Magnetic Resonance spectra were recorded on Bruker AC200 and Bruker AC250 spectrometers and continuous wave spectra on a Joel PMX-60 with positive chemical shifts referenced to TMS.

4.5.1 RUTHENIUM CYCLOPENTADIENYL COMPLEXES

**SYNTHESIS OF TETRACARBONYLBIS(\(\eta^5\)-CLOPENTADIENYL)DIRUTHENIUM**

This was done by the method of Knox, *et al.*\(^{(4-1)}\)

Triruthenium dodecacarbonyl (1.00 g, 1.56 mmol), freshly distilled cyclopentadiene (2.66 g, 40.3 mmol) and heptane (dry, deoxygenated, 70 cm\(^3\)) were refluxed, under nitrogen, for 90 minutes. The solvent volume was reduced by boiling off heptane until an orange precipitate formed then untreated heptane (50 cm\(^3\)) was added and the mixture refluxed for a further 2 hours. On cooling, the reaction mixture afforded orange crystals which were collected by filtration, then washed with \(n\)hexane (3x20 cm\(^3\)). The product was further purified by recrystallisation from heptane to yield orange crystals, 0.77 g, 74%; \(\text{IR (DCM)} \upsilon_{\text{max}} 2002\) (s), 1962 (s), 1936 (s), 1772 (s) cm\(^{-1}\); \(^1\text{H NMR} (250\text{ MHz}, \text{CDCl}_3) : \delta 5.27\) (s) ppm; \(^{13}\text{C NMR} (62.9\text{ MHz}, \text{CDCl}_3) : \delta 89.2\) (CpC), 217.6 (CO) ppm.
**SYNTHESIS OF ACETONITRILEDICARBONYL(\textit{\eta}^5-\textit{\alpha}-LOPENTADIENYL)RUTHENIUM (II) TETRAFLUOROBORATE**

Silver tetrafluoroborate (2 mmol, 0.39 g, 2.2 eq.) was washed into a Schlenk with DCM (20 cm$^3$) followed by [Ru$_2$Cp$_2$(CO)$_4$] (0.9 mmol, 400 mg), then acetonitrile (5 cm$^3$) and the mixture was stirred, under an atmosphere of nitrogen, for 24 hours. During this time a black precipitate formed which was removed by filtration then the solvent was removed \textit{in vacuo} to leave a dark solid residue which showed two peaks in the carbonyl region of the IR spectrum - 2079, 2031 cm$^{-1}$. The solid was dissolved in acetone and after filtering was layered with ether to crystallise. This yielded needle-like crystals but only in a very poor yield (few mg); IR (DCM) $\nu_{\text{max}}$ 2079(s), 2032(s) cm$^{-1}$ from carbonyl stretches; CHN : Found C 31.03; H 2.21; N 4.33; C$_9$H$_8$BF$_4$NO$_2$Ru requires, C 30.88, H 2.30, N 4.00; $^1$H NMR (250 MHz, CD$_2$Cl$_2$) : $\delta$ 2.47 (s, 3H, NCMe H), 5.70 (s, 5H, NCMe H) ppm.

**SYNTHESIS OF ACETONITRILEDICARBONYL(\textit{\eta}^5-\textit{\alpha}-LOPENTADIENYL)RUTHENIUM (II) TRIFLATE**

[Ru$_2$Cp$_2$(CO)$_4$] (294 mg) was dissolved in a minimum of DCM and filtered through a pad of activated, neutral alumina to remove any oxidised impurities. The alumina was washed with pentane and the filtrate collected was a brilliant orange colour leaving behind traces of brown impurity. The pentane was removed to leave pure [Ru$_2$Cp$_2$(CO)$_4$] (180 mg, 0.41 mmol) which was washed into a Schlenk with DCM (25 cm$^3$) and acetonitrile (25 cm$^3$). Under nitrogen, silver triflate (0.82 mmol, 210 mg, 2 eq.) was added and the mixture stirred for 20 hours in the absence of light. After this time the solution had darkened in colour and a black precipitate had formed. An IR of the solution showed that some [Ru$_2$Cp$_2$(CO)$_4$] still remained so the reaction was stirred for a further 40 hours. After this time the IR showed that all [Ru$_2$Cp$_2$(CO)$_4$] had reacted so the solution was filtered to remove the precipitate. The solvent was removed to leave a brown solid which was dissolved in a minimum of acetone and layered with ether to crystallise however no crystals formed; IR (DCM) $\nu_{\text{max}}$ 2081(s), 2034(s), 2001(s) cm$^{-1}$.
4.5.2 RUTHENIUM PENTAMETHYLCYCLOPENTADIENE COMPLEXES

4.5.2.1 LARGE SCALE SYNTHESIS OF Cp*

SYNTHESIS OF 2,3,5,6-TETRAHYDRO-2,3,5,6-TETRAMETHYL-γ-PYRONE

The protocol for this reaction followed that detailed by Fendrick, et al. (4-10)

Under an atmosphere of nitrogen, potassium hydroxide (152 g, 2.71 mol) was dissolved in methanol (950 cm$^3$) then the solution was cooled to 0°C. 3-pentanone (7.56 mol, 800 cm$^3$) was added, then acetaldehyde (30.2 mol, 1698 cm$^3$) was added dropwise, at 0°C, over a period of 15 hours. During this time the reaction mixture darkened in colour and after a further 12 hours stirring had turned dark brown / red. Cold concentrated HCl (240 cm$^3$) was then added dropwise over the period of 1 hour. The organic and aqueous layers were separated and the organic washed with HCl (2M, 1000 cm$^3$). The aqueous phase was then back extracted with ether (2x500 cm$^3$) and the organic layers were combined. The ether was then removed and the residue was washed with NaCl (2M, 500 cm$^3$) and finally the remaining methanol was removed in vacuo to leave a viscous red oil. The product was obtained by fractional distillation to yield a clear, yellow liquid, bp 69-85°C / 15 mmHg, 555.80g, (47%); IR (thin film) $v_{max}$ 1712(s) (C=O) cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$) : δ 0.92 (d, J=7 Hz, 6H, $\alpha$CH$_3$), 1.28 (d, J=7 Hz, 6H, $\beta$CH$_3$), 2.24 (m, 2H, $\alpha$H), 3.30 (m, 2H, $\beta$H) ppm.

SYNTHESIS OF 2,3,4,5-TETRAMETHYLCYCLOPENT-2-ENONE

To a flask cooled at 0°C, formic acid (2600 cm$^3$) and concentrated sulphuric acid (900 cm$^3$) were added with rapid stirring. After warming to room temp., 2,3,5,6-tetrahydro-2,3,5,6-tetramethyl-γ-pyrone (555 g, 3.56 mol) was added dropwise over 2 hours. After addition was completed the solution was warmed to 50°C for 24 hours during which time the mixture turned dark brown. After cooling, portions (500 cm$^3$) of the reaction mixture were poured into conical flasks containing ice (1000 g), then ether (500 cm$^3$) was added to each flask. The aqueous layers were separated and back extracted with ether (2x200 cm$^3$ aliquots) then the combined organic extracts were washed with NaCl (2M, 2x250 cm$^3$) portions followed by NaOH (10% w/v) until the
aqueous layer becomes alkaline. Finally, the organic layer was washed with NaCl (2M, 2x250 cm³), dried over anhydrous sodium sulphate, filtered and the ether removed by rotary evaporation. The brown residue was fractionally distilled to yield the product as a colourless liquid, 335.55 g (68%), boiling at 80-97°C; IR (thin film) v_max 1670(s), 1651(s) (C=O), 1623(m) (C=C) cm⁻¹; ¹H NMR (200 MHz, CDCl₃) : δ 1.06 (d, J=7 Hz, 3H, βCH-CH₃), 1.08 (d, J=7 Hz, 3H, αCH-CH₃), 1.58 (q, J=0.7 Hz, 3H, αC-CH₃), 1.79 (q, d, q, J=7, 0.5 Hz, 1H, βCH-CH₃), 1.89 (q, J=0.7 Hz, 3H, βC-CH₃), 2.17 (q, br, J=7 Hz, 1H, αCH-CH₃) ppm.

**SYNTHESIS OF 1,2,3,4,5-PENTAMETHYLCYCLOPENTADIENE (Cp*)**

Under inert conditions, methyllithium (0.178 mol, 127.2 cm³ of 1.4M in ether, 1.2 eq.) was transferred by cannula into a flask and cooled to 0°C. With rapid stirring, 2,3,4,5-tetramethylcyclopent-2-enone (0.148 mol, 20.50 g) was added dropwise over 30 minutes. The solution was allowed to warm to room temp. and was stirred for 18 hours. Excess MeLi was destroyed by the careful addition of methanol (50 cm³), then water (100 cm³). The resulting solution was washed with the following solution:- ammonium chloride (120 g), conc. HCl (100 cm³) and water (500 cm³) until the aqueous layer became acidic and the combined aqueous layers were back extracted with ether (200 cm³). After removal of most of the ether in vacuo the concentrate was stirred with HCl (6M, 2 cm³) for 1 hour to ensure water elimination from intermediate. Finally, the ether concentrate was washed with sodium hydrogencarbonate (5% w/v, 100 cm³), dried over anhydrous potassium carbonate and filtered. The remaining ether was then removed and the product was obtained by fractional distillation yielding a pale yellow liquid, 12.54 g (62%), boiling at 65-70°C / 15 mmHg; IR (thin film) v_max 1659(s) (C=C) cm⁻¹; MS (+EI) : M=136. Other peaks 121, 105, 91, 77; Accurate mass, Found 136.12570; C₁₀H₁₆ requires 136.12520; Deviation = 3.69 ppm; ¹H NMR (250 MHz, CDCl₃) : δ 1.02 (d, J=7.5 Hz, 3H, CH-CH₃), 1.79 (2d, J=0.8 Hz, 6H, C-CH₃), 1.83 (2d, J=0.4 Hz, 6H, C-CH₃), 2.50 (eq, J=8 Hz, 1H, CH=CH₃) ppm; ¹³C NMR (62.9 MHz, CDCl₃) : δ 10.90 (C-CH₃), 11.39 (C-CH₃), 13.91 (CH-CH₃), 51.34 (CH-CH₃), 134.00 (C-CH₃), 137.58 (C-CH₃) ppm.
When this synthesis was repeated on a larger scale the IR of the product after distillation showed a large peak at ~1700 cm\(^{-1}\) due to a carbonyl impurity. The product was purified by column chromatography (silica, 100 g) using elution with \(n\)hexane to collect the product, the impurity remaining bound to the silica.

### 4.5.2.2 SYNTHESIS OF RuCp* STARTING COMPLEXES

#### SYNTHESIS OF DI-\(\mu\) -CHLORO-BIS[(\(\eta^5\)-PENTAMETHYLCYCLOPENTADIENYL)CHLORORUTHENIUM(III)]

This followed the procedure reported by Koelle & Kossakowski.\(^{(4-2)}\)

To a filtered solution of hydrated ruthenium trichloride (4.0 g, 15.8 mmol) in methanol (100 cm\(^3\)), 1,2,3,4,5-pentamethylcyclopentadiene (36 mmol, 4.8 g, 5.52 cm\(^3\)) was added in inert conditions. The mixture was refluxed for 4 hours then cooled at -77°C for 2 hours which produced a black precipitate. This was filtered off and washed with pentane to yield a black microcrystalline solid 2.60 g (54%). The filtrate and washings were refluxed for a further 4 hours and cooled but no more product was obtained; CHN : Found C 40.15, H 4.96, N 0; \(\text{C}_{20}\text{H}_{30}\text{Cl}_{4}\text{Ru}_{2}\) requires C 39.10, H 4.92, N 0; IR (KBr disc) \(\nu_{\text{max}}\) 2910(w), 1447(br,$\delta$), 1370(s), 1181(w), 1074(w), 1023(s) cm\(^{-1}\); \(^{1}\text{H NMR}\) (200 MHz, CDCl\(_3\)) : \(\delta\) 4.37 (br,$\delta$, Cp*CH\(_3\)) ppm.

#### SYNTHESIS OF TETRA-\(\mu\) -CHLORO-TETRAKIS[(\(\eta^5\)-PENTAMETHYLCYCLOPENTADIENYL)RUTHENIUM(II)]

The method described by Fagan, \textit{et al},\(^{(4-3)}\) was used for this synthesis.

\([\text{Cp}^{*}\text{RuCl}_2]_2\) (1.02 g, 1.66 mmol) was dissolved in THF (10 cm\(^3\)), in inert conditions, to give a brown solution. To this, lithium triethylborohydride (3.32 mmol, 3.32 cm\(^3\) of 1.0M in THF, 2 eq.) was added all at once. Gas was evolved upon addition and after stirring for 1 hour the solution was cooled and an orange precipitate formed. This was collected by filtration then washed with THF and \(n\)hexane to yield an orange microcrystalline solid, 0.44 g (50%); CHN : Found C 43.07, H 4.90, N 0; \(\text{C}_{40}\text{H}_{60}\text{Cl}_{4}\text{Ru}_{4}\) requires C 44.20, H 5.56, N 0; \(^{1}\text{H NMR}\) (200 MHz, d\(_6\)-acetone) : \(\delta\) 3.80 (s, Cp*CH\(_3\)) ppm.
SYNTHESIS OF TRISACETONITRILE(η 5-NITRAMETHYLCYCLOPENTADIENYL)RUTHENIUM (II) TRIFLATE

The method described by Fagan, et al., was used for this synthesis. [RuCp*Cl]4 (1.21 g, 1.11 mmol) was dissolved in MeCN (10 cm³). This mixture was refluxed for one hour then allowed to cool to room temperature. To this solution, silver(I) triflate (1.14 g, 4.45 mmol, 4 eq.) was added and a white precipitate formed immediately. The solution was filtered to remove AgCl, then dried in vacuo. To the residue, ether (10 cm³) was added and the orange solid (1.83 g, 81%) was collected by filtration and dried.

\[ {^1}H \text{ NMR (250 MHz, d}_{6}\text{-acetone) } \delta 1.62 (s, 15H, C-CH}_3, 2.43 (br, 9H, NCCH}_3). \]

4.5.3 REACTIONS OF GUANIDINES WITH RuCp* COMPLEXES

REACTION OF [Cp*RuCl2]2 WITH TRI-p-TOLYLGUANIDINE

A generic example of a reaction of this type is as follows. [Cp*RuCl2]2 (0.99 g, 1.61 mmol), tri-p-tolylguanidine (2.12 g, 6.44 mmol, 2 eq. per Ru) and toluene (20 cm³) were stirred at room temperature, under an atmosphere of nitrogen, for 24 hours. After this time, the orange solution obtained was filtered through celite. Storage of the filtrate at 5°C did not yield any solid material, therefore the toluene was removed to dryness and the residual solid dissolved in DCM (5 cm³). This clear, orange solution was layered with hexane though diffusion of the solvents did not yield any crystalline material.

The solvent was removed in vacuo and the residue dissolved in DCM. Spot TLC on the solution using ethyl acetate as eluent showed that two compounds exist in the solution, one a fast moving orange component, the other a slower moving colourless one. Column chromatography (silica gel) using ethyl acetate as eluent caused an orange band to move on the column though this gradually changed colour to green and its movement slowed. This band was eventually eluted off the column and inspection by \[ {^1}H \text{ NMR (250 MHz, CDCl}_3\) revealed this to be a mixture of products.\]
Chapter Four 

Reactions with Ruthenium Half-Sandwich Complexes

REACTION OF [Cp*RuCl]₄ WITH TRI-p-TOLYLGUANIDINE

To [Cp*RuCl]₄ (219 mg, 0.20 mmol), tri-p-tolylguanidine (0.53 g, 1.61 mmol, 8 eq.) was added with toluene (20 cm³). A green solution formed immediately and persisted after 16 hours stirring at room temperature. Isolation of the precipitate (285 mg, 4eq. guanidineHCl = 295 mg) left a clear solution from which no crystals could be grown. The solvent was removed in vacuo, the residue dissolved in DCM and triphenylphosphine (209 mg, 0.80 mmol, 4 eq.) added. The reaction mixture turned yellow upon stirring at room temperature for 3 hours. DCM was removed to dryness, leaving a yellow solid which was soluble in ether though not hexane. The solid was redissolved in DCM (5 cm³) and layered with hexane (20 cm³) though no crystalline material was obtained. No spectroscopic data was obtained for this product.

SYNTHESIS OF [(η⁵-Cp*)Ru(η⁶-p-TOLYL)NC(HN-p-TOLYL)₂][SO₃CF₃] 41

To [Cp*Ru(NCMe)₃][OTf] (386 mg, 0.759 mmol), tri-p-tolylguanidine (0.250 g, 0.759 mmol) was added with THF (10 cm³). The mixture was heated under reflux for 6 hours, cooled to room temperature and filtered. Ether (10 cm³) was added causing a white precipitate to crash out of solution. All solvent was removed, then the residue dissolved in THF (8 cm³) and layered with ether (25 cm³). Diffusion of the solvents at room temperature yielded a crop of colourless crystals 41 (67 mg, 12% unoptimised); ¹H NMR (250 MHz, CDCl₃) : δ 1.75 (br s, 15H, Cp*CH₃), 5.2 (br d, 4H, ArH), 6.9 – 7.1 (cm, 8H, ArH), 7.63 (br s, 2H, NH) ppm; ¹³C NMR (62.9 MHz, CDCl₃) : δ 9.89 (Cp*CH₃), 17.74 (Ar-CH₃ coordinated), 20.61 (ArCH₃ uncoordinated), 81.26, 86.48, 93.95, 95.46 (ArC coordinated), 121.80, 129.04, 132.86, 136.10 (ArC uncoordinated), 151.25 (quat, CN₃); CHN : C₃₃H₃₈N₃F₃O₃SRu requires C 55.45, H 5.36, N 5.88; Found C 55.66, H 5.47, N 6.02; MS (+ve FAB) : m/z 566 (molecular ion), 329 (tri-p-tolylguanidine).

Crystal Data for 41.

Data were collected using Mo-Kα radiation on a colourless block of dimensions 0.58 x 0.16 x 0.12 mm on a Stoe Stadi4 diffractometer in the range 6≤2θ≤48° using the ω-θ method. Of a total of 6361 reflections collected, 4425 (Rint =
were independent. The structure was solved by direct methods (SHELXTL)\(^{4-16}\). Hydrogen atoms were located in the difference map and refined subject to the restraint that the N-H distances are equal. The final difference-map extrema were 0.429 and -0.323 e \(\text{Å}^{-3}\) giving a final \(R\) of 0.0517 for 411 parameters.

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*Table 4.3. Crystallographic data for 41.*

The reactions of stoichiometry 2:1 and 3:1 (Ru: guanidine) were performed using exactly the same procedure. However, upon dissolution of the ether and THF solution no crystals were obtained.

### 4.5.4 REACTIONS WITH RUTHENIUM ARENE COMPLEXES

These reactions were followed the protocol reported for the synthesis of \([\text{Ru}(\eta^1-\text{MeC}_6\text{H}_4\text{Pr-p})\{\eta^2-(\text{NPh})_2\text{CNHPh}\}\text{Cl}]^{4-7}\)

**REACTION WITH TRICYCLOHEXYLGUANIDINE**

Tricyclohexylguanidine (362 mg, 0.59 mmol) and \([\{\text{Ru}(\eta^1-\text{MeC}_6\text{H}_4\text{Pr-p})\text{Cl}\}_2\}]^{2}\) (722 mg, 2.36 mmol) were added to a Schlenk with toluene (20 cm\(^3\)). The resulting mixture was stirred at room temperature, under nitrogen, for 48 hours. The resulting orange solution was filtered to remove the white precipitate formed in the reaction. The filtrate was reduced in volume to dryness and attempts were made to crystallise the residual orange solid from DCM / hexane mixtures by slow
evaporation of the solvent. However, no crystalline material was obtained from the reaction.

The reaction was repeated on a similar scale and again an orange solution formed after stirring at room temperature. Following filtration, the orange solution was split into two aliquots both of which were purified by column chromatography.

Following reduction in solvent volume to a few ml, the orange solution was loaded onto a column of silica gel. Initially, elution with hexane caused an orange band to move down the column though this began to change colour and it’s movement slowed. The band eventually turned green and stopped moving altogether. Elution with more polar solvents (toluene, DCM, ethyl acetate and ethanol) did not move this band any further down the column.

The second aliquot was similarly reduced in volume before loading onto an alumina column. Elution with hexane also caused an orange band to run down the column though this quickly turned green and stopped on the column. Elution with more polar solvents again failed to remove this band from the column.

**REACTION WITH TRIISOPROPYLGUANIDINE**

The reaction of triisopropylguanidine with \([\{\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr-p})\text{Cl}_2\}\}_2]\) and crystallisation of the product was carried out by Marie Elliot, an Honours student working under my supervision.

Triisopropylguanidine and \([\{\text{Ru}(\eta\text{-MeC}_6\text{H}_4\text{Pr-p})\text{Cl}_2\}\}_2]\) were added together and toluene added. The mixture was stirred at room temperature, under nitrogen, for 24 hours. The resultant mixture was filtered and the filtrate dried in vacuo. The orange solid obtained was crystallised from DCM / hexane by slow evaporation of the solvents, yielding large red crystalline blocks 42.

**Crystal Data for 42.**

Data were collected using Mo-Kα radiation on a red block of dimensions 0.35 x 0.31 x 0.19 mm on a Stoe Stadi4 diffractometer in the range 5≤2θ≤55° using the o-θ method with learnt profile. Of a total of 12740 reflections collected, 5113 (R_{int} = 0.0227) were independent. The structure was solved by direct methods (Sir 92). The hydrogen atom on N(3) was located in a difference synthesis and
refined freely. The final difference-map extrema were 0.455 and -0.380 e Å\(^{-3}\) giving a final \(R\) of 0.0274 for 240 parameters.

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*Table 4.4. Crystallographic data for 42.*

**REACTION WITH TRIS((S)-(−)-\(\alpha−\text{METHYLBENZYL})\)GUANIDINE**

Tris((s)-(−)-\(\alpha−\text{methylbenzyl})\)guanidine (1.056 g, 2.84 mmol) and \([\{\text{Ru}(\eta-\text{MeC}_6\text{H}_4\text{Pr-}p)\text{Cl}_2\}_2\}\) (435 mg, 0.71 mmol) were washed into a Schlenk with toluene (20 cm\(^3\)). The resultant mixture was stirred for 48 hours at room temperature, under an atmosphere of nitrogen. The reaction mixture was filtered to remove the guanidine salt and the filtrate dried *in vacuo* to leave a sticky orange oil. Dissolution of this oil in DCM and layering with hexane did not yield any crystalline material. The solvents were removed to dryness and the residual oil dissolved in the minimum of DCM. Spot TLC (silica gel) of this solution with ethanol as eluent showed two spots, one fast moving orange spot and one slower moving brown spot. Preparation TLC (silica gel) was then attempted to purify the product. Elution with ethanol separated an orange species from the brown which remained on the baseline. The orange coloured silica gel was scraped off the plate and Soxhlet extraction into ethanol under nitrogen was attempted. However, no product was recovered in the ethanol.
4.6 REFERENCES

CHAPTER FIVE

REACTIONS WITH GROUP IV METALS

5.1 INTRODUCTION

The reactions of substituted guanidines with various early transition metal complexes were studied with an interest in assessing how guanidines would behave as ligands with larger, more electropositive metals. There was still some hope that a complex containing a tridentate guanidinate ligand could be synthesised and it was felt that reaction with larger metal centres would increase the likelihood of this occurring. However, even if this goal was not realised it was hoped that complexes with other interesting properties could be obtained. For example, complexes of Group IV metals which contain bidentate nitrogen ligands in their coordination sphere have been utilised as potential “next generation” olefin polymerisation catalysts. Numerous examples of these have recently been published including some examples with ligands isostructural to guanidinates.\(^5\)

In addition complexes of titanium with guanidinate ligands may have potential as precursors to titanium nitride films, as used in the semiconductor industry.\(^{\text{5-4}}\) Presently, it is highly problematic to produce TiN of sufficient purity for this application. Therefore any novel complexes of this type would be of interest to study as precursors.

In terms of the behaviour of guanidinates as ligands, complexes of early transition metals would be of interest to give further insights to the ligand properties of the compounds. Of particular interest would be further evidence of the guanidinate ligand delocalising in order to stabilise a metal in a higher oxidation state, behaviour that was first observed in a series of molybdenum dimers.\(^{\text{5-5}}\)
5.2 Reaction with Titanium Tetraakisdimethylamide

The first reactions of guanidines attempted with early transition metals were those of tri-alkylguanidines with titanium tetraakisdimethylamide [Ti(NMe₂)₄]. In these reactions it was hoped that the guanidines would be acidic enough in order to be doubly deprotonated by the basic dimethylamido ligands. This would then result in the liberation of dimethylamine from solution with the formation of a titanium guanidinate complex. (5-6,5-7,5-8) Although less acidic than aryl substituted guanidines, tri-alkylguanidines were used first of all to try to limit the number of ligands able to coordinate to the titanium centre. This is due to their increased steric demand (in comparison to planar aryl ligands) which would hopefully lead to tetrahedral geometry around the metal centre. The main reason for attempting to restrict the coordination of the titanium centre was that tetrahedral titanium complexes were known to be more volatile than octahedral. (5-9) The potential volatility of these complexes would then be utilised in order to see if they did behave as chemical vapour deposition precursors. It was viewed as plausible that guanidinate complexes could behave as precursors due to the known fragility of the central CN₃ core. For example, during mass spectroscopy, the majority of guanidine containing compounds, both free ligands and complexes, fragmentation of the guanidine occurs with the main peaks being observed due to daughter carbodiimde and amine peaks. With some speculation, reaction pathways exist which could result in the formation of titanium and nitrogen species.

[Ti(NMe₂)₄] is a highly air and water sensitive compound, which exists as an orange oil at room temperature. (5-10) Though it can be stored for a period of time under nitrogen, it is most easily handled as a standard solution. The [Ti(NMe₂)₄] used in these reactions was kindly provided by Dr. Colin Pulham. To facilitate it’s handling under an inert atmosphere, a 0.267 moldm⁻³ solution in toluene was prepared. This proved a more than satisfactory method of storing and manipulating the compound.
Chapter Five

5.2.1 Reaction of [Ti(NMe)] with trialkylguanidines

The first reaction attempted was that of tricyclohexylguanidine with [Ti(NMe)_4]. The reaction was performed in a 2:1 molar ratio with a view to producing a four coordinate titanium complex containing two dianionic chelating guanidinate ligands (Fig. 5.1).

The reaction was performed in toluene solution and upon addition of the [Ti(NMe)_4] to the guanidine the colour of the solution deepened from its initial yellow through orange to red. After stirring at room temperature, the solvent was removed to yield a sticky, red solid. This solid was very soluble in hexane and the resulting solution was filtered to give a clear, red solution. Attempts were made to obtain crystalline product by storing the solution for extended periods at 5°C and -30°C though no crystalline material was obtained. During storage at -30°C the solution started to decompose, as evidenced by the loss of colour in the solution and formation of a white precipitate (presumed to be TiO_2). This prevented any attempts to characterise the products of the reaction.

A reaction of similar stoichiometry was also attempted with other trisubstituted guanidines. With the triisopropyl derivative, addition of [Ti(NMe)_4] to the guanidine solution again caused the solution to deepen in colour from yellow to orange. The reaction mixture was left stirring in toluene overnight and the solution

![Figure 5.1. Reaction of [Ti(NMe)] with two equivalents of trisubstituted guanidine.](image-url)
deepened further to red during this time. Removal of the solvent left a sticky oil and a $^1$H NMR spectrum of this showed a number of different peaks corresponding to the Pr groups, indicating that a mixture of products was obtained. As an attempt to see if the reaction would proceed further, the mixture was dissolved in toluene and warmed for a short period. The only effect that this had was to cause the material to decompose and a pale coloured precipitate formed.

With there being a mixture of products formed in the reaction, the reaction was repeated though this time the [Ti(NMe$_2$)$_4$] was introduced to the guanidine dropwise at -78°C. This was done in an attempt to lessen the excess of [Ti(NMe$_2$)$_4$] present in the reaction mixture and also to slow the rate of reactions taking place. It was hoped that this would alter the formation of products to produce only one major product. After addition was complete the solution was seen to be orange in colour already. The mixture was allowed to warm to room temperature before the solvent was removed. Attempts were made to crystallise the red solid from hexane solution though these proved unsuccessful, with the product proving to be highly soluble in hexane. The high solubility of the red solid in hexane indicated that the complex was neutral and so purification was attempted by sublimation. With gentle warming under vacuum white needles formed on the cold finger. This solid melted at 57-58°C confirming it was free ligand. Raising the temperature caused no further solid to sublime until at 150°C the red solid started to decompose.

From these initial reactions, it was apparent that a reaction was occurring between the [Ti(NMe$_2$)$_4$] and the trisubstituted guanidines. The products of these reactions were all extremely soluble in hexane, which was encouraging in that it would be expected that complexes containing alkyl substituents would have a high degree of solubility in non-polar solvents. However, from a purification point of view, their solubility was proving a problem in attempts to crystallise the product. A further feature of this problem may be that more than one complex is forming in the reactions, further depleting the likelihood of crystallisation occurring.

In an attempt to reduce the solubility of product complexes, the reaction was repeated using tri-$p$-tolylguanidine. Previous experience with aryl substituted
guanidines showed them to be less soluble than alkyl guanidines and so more readily crystallised.

5.2.2 REACTION WITH TRIARYLGUANIDINES

The standard solution of $[\text{Ti(NMe}_2]_4$ was further diluted in toluene while the guanidine was dried before dissolving in toluene. Both solutions were cooled to $-78^\circ \text{C}$ then the guanidine was added dropwise to the $[\text{Ti(NMe}_2]_4$ via a cannula. As soon as addition commenced, a deepening of the solution colour was observed. This apparent higher rate of reaction was expected as an aryl substituted guanidine would react more rapidly than an alkyl substituted one. This is because the first step in the reaction would involve abstraction of a proton from the amine groups of the guanidine. In other words, while not being acidic, the amine protons in an aryl guanidine are more acidic than those in an alkyl guanidine. From the resulting solution a dark red solid was obtained and following redissolution in hexane and filtration a clear, deep red solution was obtained. The solid reaction product was again found to be very soluble in hexane and all attempts to crystallise the material failed.

The reaction was repeated using one equivalent of guanidine to titanium. The reaction would occur in a similar manner although it was expected that some NMe$_2$ ligands would remain coordinated to the metal centre (see Fig. 5.2).^{5-6}

![Figure 5.2. Reaction with one equivalent of guanidine.](image-url)
Addition of the guanidine in toluene to the [Ti(NMe₂)₄] resulted immediately in the formation of an orange coloured solution. Following warming to room temperature, evaporation of the solvent to dryness, dissolution of the resultant solid in the minimum volume of hexane and filtration a bright orange solution was obtained. Attempts to crystallise this product at various temperatures and concentrations failed and again no spectroscopic data was obtained.

Following these experiments of reacting [Ti(NMe₂)₄] with various tri-substituted guanidines it became apparent that while reaction between the two compounds proceeded readily isolation of a product proved problematic. The source of this problem may be twofold; the reaction does not yield a majority product and so crystallisation is hampered or, the products formed in the reactions are so soluble that they remain in solution even when concentrated. It was decided that while it may be possible to alter the reaction conditions in order to minimise production of different complexes, the problem of solubility would still remain. For this reason the next set of reactions concentrated on the introduction of ligands which would reduce the solubility of the product complexes.

5.3 REACTIONS WITH TITANIUM TETRACHLORIDE

TiCl₄ was chosen as a starting material as it had the advantages of being readily available and it was known to react with lithiated amidinates. Although difficult to handle in its pure state, its handling was facilitated by using it as a standard solution in hexane. One disadvantage of using TiCl₄ compared to [Ti(NMe₂)₄] is that as the guanidine needs to be deprotonated in order to react with the TiCl₄, so introducing an additional step into the reaction protocol. The guanidines were typically deprotonated with nBuLi so producing LiCl as a by-product in the reactions. The formation of this introduces a further step in the experiment in that the LiCl is required to be removed from the reaction mixture before crystallisation could be attempted.
5.3.1 Reaction with Trialkylguanidines in THF

The first reaction attempted was that of TiCl₄ with two molar equivalents of monolithiated triisopropylguanidine (see Fig. 5.3).

\[
\text{MCl}_4 + 2 \left[ \begin{array}{c}
NR \\
RN \\
NHR
\end{array} \right] \text{Li}^\ominus \rightarrow 2 \text{LiCl} + \left[ \begin{array}{c}
RHN \\
N
\end{array} \right]
\]

Figure 5.3. Reaction of TiCl₄ with monolithiated guanidine

The anticipated product from this reaction contains the Ti chelated by the two monoanionic guanidinate ligands with two chloride ions completing the coordination sphere of the metal. The presence of the residual chlorides (if this product was obtained) would serve to reduce the solubility of the complex in hexane so promoting the likelihood of crystallisation.

The first step of the reaction, the deprotonation of the guanidine proceeded smoothly in THF. The TiCl₄ was then added to the guanidinate at -78°C which resulted in an instant colour change producing a brown solution and a light coloured precipitate. Following warming to room temperature and removal of the solvent, attempts were made to dissolve the residual solid in hexane and toluene. These proved unsuccessful and as the reaction mixture appeared to be steadily decomposing, it was discarded without analysis.

This reaction was repeated though this time the TiCl₄ was added to two molar equivalents of the doubly deprotonated dilithiotriisopropylguanidinate (see Fig. 5.4)

\[
\text{MCl}_4 + 2 \left[ \begin{array}{c}
NR \\
RN \\
NHR
\end{array} \right] \text{Li}^\ominus \rightarrow 2 \text{LiCl} + 4 \text{LiCl} + \left[ \begin{array}{c}
R \end{array} \right]
\]

Figure 5.4. Reaction of TiCl₄ with doubly deprotonated guanidine.
Analogous to the previous reaction, upon addition of TiCl$_4$ to the guanidinate, an immediate colour change was observed. Following warming to room temperature the solution was a dark brown colour and a light coloured precipitate was also present. Filtration yielded a deep red solution which was dried in vacuo to give an oily solid. This was redissolved in hexane to give a clear solution and a $^1$H NMR spectrum revealed that the product contained iPr groups (characteristic doublets and septets) but gave little further information as the instrument was poorly shimmed. With the ready solubility in hexane indicating that a neutral complex(es) had been formed in the reaction, purification was attempted by vacuum sublimation. After removal of the solvent, warming under vacuum resulted in white needles collecting on the cold finger. These were again thought to be the free ligand. Further heating caused the colour of the oil to darken from red through to brown/black, doubtless as a result of decomposition.

5.3.2 Reaction with Trialkylguanidines in Hexane

This reaction was repeated, the only change being the use of hexane as the reaction solvent instead of THF. Following lithiation of the guanidine, warming of the solution to room temperature caused a white precipitate to form. This phenomenon had previously been observed during the dilithiation of guanidines and was thought to result from the reaction between the guanidine and the - BuLi proceeded towards completion as the temperature was raised. After cooling the resultant mixture to -78°C, TiCl$_4$ was added and an immediate colour change occurred. The colour change indicated a reaction had occurred though it was not apparent that the solid was being consumed in the reaction. However, this may be due to the formation of LiCl in the reaction masking the consumption of the lithiated guanidine. After addition was completed the reaction mixture was allowed to warm to room temperature then stirred for two hours. The reaction mixture was then filtered separating the dark red solution from the light coloured precipitate. In an attempt to crystallise the product the volume of solvent was reduced to a minimum though again no crystalline solid was obtained.
Once again in these experiments reaction appears to have occurred between the guanidinate and the Ti starting complex. However, crystallisation again proved difficult whether due to there being more than one product formed in the reactions or the solubility of the product complexes being too great, even in hexane. However, reacting TiCl₄ with the monolithiated guanidinate resulted in a product which was insoluble in hexane and toluene. This was encouraging in that it was hoped that by incorporating halides into the product it would reduce the solubility of the products. However, no crystalline material was obtained from these reactions and so further modification of the synthetic strategy was required.

Therefore, in the next series of reactions the titanium was introduced to the reaction in the form of tetrachlorobis(tetrahydrofuran)titanium [Ti(thf)₂Cl₄]. This was done in an effort to predict the geometry of the product complex (octahedral) while still maintaining halides in the product complex. This was done in an attempt to reduce the number of products forming in the reaction as guanidines were known to be capable of acting as ligands in many different modes. This versatility may be a problem in these reactions by allowing more complexes to form in the reaction (see Fig. 5.5 for one possibility), and inhibiting crystallisation of the desired product. Further products may also result from the reduction of Ti(IV) to Ti(III) which may introduce yet more impurities.⁵⁻¹²

5.4 Reaction with Tetrachlorobis(tetrahydrofuran)Titanium

Tetrachlorobis(tetrahydrofuran)titanium [Ti(thf)₂Cl₄] is a brilliantly coloured yellow solid which is air sensitive.⁶⁻¹³ It is an attractive starting material as the labile tetrahydrofuran ligands makes it reactive as well as soluble in a variety of solvents.

It had been used previously in reactions with monolithiated amidinates and in these, the labile tetrahydrofuran and two of the chloride ligands were substituted
for two chelating amidinates.\(^{5-14}\) The product complex retained two chloride ligands and its overall octahedral geometry. It was anticipated that guanidines would react in a similar manner to this thus producing a complex containing two monoanionic chelating guanidinates (see Fig 5.6).

**Figure 5.6. Reaction of Trisubstituted guanidine with [Ti(thf)\_2Cl\_4]**

8.4.1 **REACTIONS WITH TRISUBSTITUTED GUANIDINES**

The first reaction attempted was [Ti(thf)\_2Cl\_4] with monolithiated triisopropylguanidine in ether. The guanidine was deprotonated by reaction with nBuLi at -78°C and the resulting solution was cannulated into a suspension of [Ti(thf)\_2Cl\_4] in ether. An immediate colour change was observed upon the addition of the guanidinate and as the new red colour strengthened, it was noticeable that the [Ti(thf)\_2Cl\_4] was being consumed in the reaction. After addition was completed warming to room temperature yielded a deep red solution with a pale precipitate. The solution was filtered then the solvent was removed \textit{in vacuo} leaving a purple/red solid. This solid proved only slightly soluble in hexane which suggested that chloride ligands remained on the titanium centre as anticipated. After drying to remove the
hexane the solid was taken up in ether and some insoluble precipitate from decomposition was filtered off leaving a clear red solution. A portion of this solution was dried and inspected via $^1$H NMR. The resulting spectrum was very promising in that signals were observed for the CH$_3$ and CH groups of the isopropyl function on the guanidinate ligands.

Buoyed on from this, various attempts were made to crystallise a product from the red solution. Initial attempts focussed on concentrating the ether solution of the product. The main problem encountered with this was that every time the solvent volume was reduced some precipitate formed which would not redissolve upon warming. This seemed to be as a result of some decomposition occurring during manipulation. A clear solution was eventually obtained though upon cooling the solution only a pale precipitate formed.

The reaction was repeated using some of the other trisubstituted guanidines available, namely tricyclohexyl and triphenylguanidine. Both of these were singly deprotonated and reacted with [Ti(thf)$_2$Cl$_4$] in 2:1 stoichiometry. In both cases reaction was carried out in ether at -78°C with a solution of the guanidinate added to a suspension of the [Ti(thf)$_2$Cl$_4$] and as for the initial reaction an immediate colour change from yellow solid to red solution was observed. With the tricyclohexylguanidinate, purification was attempted by concentrating the reaction mixture before filtering through celite. However, even though extreme care was taken in this procedure some precipitate formed immediately following filtration. This occurred on many occasions and eventually led to all product being lost without any crystalline material being obtained.

A similar problem was encountered with the triphenylguanidinate ligand. Following addition and warming to room temperature, a bright red solution with pale precipitate was obtained. The solvent volume was again reduced and upon filtration further white precipitate was produced. Eventually a clear solution was obtained though attempts to crystallise this by cooling failed. Hexane was then carefully added to the ethereal solution to the point that some precipitate formed though this did not redissolve upon gentle warming of the mixture and attempts to remove the precipitate by filtration also failed.
At this time, the pursuit of a crystalline product was proving extremely elusive. In most of the experiments that had been attempted reaction appeared to have proceeded though in every case crystallisation proved fruitless. Attempts had been made to vary both the starting titanium complex and ligand substituents in an effort to influence the product obtained from reaction. However, for whatever reason, no crystalline material could be isolated. As there seemed to be no obvious way to further dictate the titanium environment in the reaction (from what had already been done) it was decided to limit the reaction possibilities of the ligand. By way of explaining this, if we consider a monodeprotonated guanidinate, there remains a possibility that a further deprotonation could occur, forming a dianionic ligand. This could have an effect on the products of a reaction by introducing by-products which would hamper the attempts to crystallise the major product. There is no evidence that this did happen as the main tool for examining reaction solutions, $^1$H NMR, was not suitable for detecting differences between the two types of ligands if present.

One method of preventing this happening altogether would be to remove the opportunity for the guanidinate to undergo a further deprotonation. This was done by using the tetrasubstituted guanidine, diethyldiphenylguanidine, in which only one amine proton exists and so can only form a monoanionic species.

### 5.4.2 Reactions with a Tetrasubstituted Guanidine

Reactions of $[\text{Ti(thf)}_2\text{Cl}_4]$ with diethyldiphenylguanidine were carried out in an identical manner to those with the trisubstituted guanidines. In the first reaction the guanidine was deprotonated with $n$BuLi in ether solution at -78°C. The mixture was then warmed to room temperature to ensure complete reaction had occurred before being cooled to -78°C again. This solution was added to a suspension of $[\text{Ti(thf)}_2\text{Cl}_4]$ in ether and upon addition, an immediate colour change was observed. Following addition, a red/purple solution was obtained and a pale precipitate formed as the yellow $[\text{Ti(thf)}_2\text{Cl}_4]$ was consumed in the reaction. Filtration yielded a clear red/purple solution from which a dark orange solid was obtained upon drying. A $^1$H NMR spectrum was obtained of this solid which proved to be very promising as two signals were observed which were possibly due to the CH$_2$ and CH$_3$ groups of the
ethyl functions corresponding to free and bound ligands. Even more encouraging was that a red crystalline material had formed from the aliquot of reaction product separated for the NMR.

In an effort to obtain a single crystal for X-ray study the mother solid was redissolved in the minimum volume of ether, filtered and the resulting clear solution was stored at -30°C for a few days. No crystals were obtained during this time and during subsequent manipulation the solid decomposed.

Although the crystalline material obtained from the aliquot was not of very high quality an attempt was made to collect its X-ray diffraction pattern. Unfortunately, no diffraction peaks were obtained from any of the material mounted in the diffractometer.

However, some of this material was salvaged for further ¹H NMR study. The resulting spectrum confirmed the presence of the free ligand (identical doublet and septet peaks and chemical shifts) while it also contained signals with similar peaks, shifted upfield from those observed for the free ligand. This would indicate that the ligand is gaining electron density following deprotonation and complexation which is surprising as the opposite trend would be expected.

This had been the promising reaction so far in that crystalline material had been obtained and also the NMR spectrum showed a clear shift in the peaks of the free ligand. Therefore, the combination of restricting the deprotonation of the guanidine as well as maintaining halides in the complex has resulted in a major product forming with reduced solubility. Therefore, this reaction was repeated in order to obtain single crystals of suitable quality for X-ray diffraction study.

The reaction was repeated in an identical manner and was observed to react in a similar fashion. After filtering the solution to remove LiCl, crystallisation was attempted from cooling the reaction solution. Some red precipitate formed during this time but unfortunately nothing crystalline. The solid was collected by filtration and ¹H NMR confirmed this to be the same as the crystalline material obtained in the previous reaction. In an attempt to slow the crystallisation process down, the again free from precipitate filtrate was stored at -30°C but the Schlenk was insulated to
reduce the rate of cooling. Again a red precipitate was obtained in the reaction but was not crystalline.

A further repeat was carried out and this time the reaction solution was decanted from the precipitate. The ether solvent was removed to dryness and the dark red residue was dissolved in a small amount of toluene giving a bright red solution. This was in turn filtered and stored at 5°C to crystallise. After a short period red crystalline needles had formed although once again they were not of sufficient quality and no diffraction peaks were observed.

The solution was once again filtered removing all precipitate and the clear solution was stored at 5°C. Over the period of a few weeks red needles (ca. 20%) formed again and at first these appeared to be of better quality than those previously obtained. Indeed, when mounted in a beam of X-rays diffraction peaks were observed and diffraction data were collected. The structure of the complex was solved and confirmed the complex as $[\text{Ti} \{(\text{PhN})_2\text{CNEt}_2\}_2\text{Cl}_2]$ (Fig. 5.7) containing a six coordinate titanium (IV) centre, ligated by two monoanionic chelating guanidinate ligands and two chlorides with a molecule of toluene also in the unit cell.

In the crystal structure both the guanidinate ligands are equivalent and this was confirmed from the $^1\text{H}$ and $^{13}\text{C}$ NMR spectra which have only one resonance per equivalent nucleus in the ligand. In the $^1\text{H}$ NMR, the triplet resulting from the methyl groups of the ethyl substituents are shifted from 1.16 to 0.84 ppm. Similarly, the quartet arising from the methylene groups was shifted from 3.33 to 2.64 ppm. The peaks arising from the phenyl substituents are different in shape though are in an identical range of chemical shifts. In the $^{13}\text{C}$ spectrum, the peaks from the ethyl substituents have moved in a similar manner, from 12.7 and 41.8 to 12.2 and 42.2 ppm respectively. These upfield shifts of the ethyl substituents is surprising as the signal from the central quaternary carbon of the CN$_3$ unit has shifted downfield from 150.0 to 165.5 ppm. This is indicative of a loss of electron density from the ligand as a result of deprotonation and coordination, a similar effect that has been observed previously. A satisfactory elemental analysis of the crystals was also obtained.
Figure 5.7. Molecular structure of [Ti{(PhN)$_2$CNEt$_2$)$_2$Cl$_2$} 51.
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Reactions with Group IV Metals

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Table 5.1. Selected bond lengths (Å) and angles (°) for 51.

In the solid state the complex adopts a distorted octahedral coordination geometry. The distortion arises from the restricted bite angle [63.39°] imposed by the chelating guanidinate ligands. However, the structure of 51 is very similar to the corresponding amidinate complex, [Ti{PhC(NSiMe3)2}2Cl] which also contains a titanium centre coordinated by two chelating amidinates and two chlorides. The only major difference between the complexes is that the guanidinate is symmetrically bound to the titanium [Ti-N 2.056(4) Å] whereas as the amidinate is not [Ti-N 2.066(5) Å and Ti-N(1) 2.106(5) Å]. As has been observed for other guanidinate ligands, the angles around the central CN3 core [108.1(4), 125.5(4) and 126.4(4)°] total 360°, indicating a strict planarity at the centre of the guanidinate and delocalisation of electron density within the ligand. Also of note within the CN3 core is the reduced angle between the two coordinating nitrogens [108.1(4)° for N(1)-C(1)-N(2) vs. 125.5(4)° and 126.4(4)° for N(1)-C(1)-N(3) and N(2)-C(1)-N(3)] giving an indication of the geometric restriction that the guanidinate is under when coordinated.

Following on from this reaction, one interesting experiment would be to react the complex with methyllithium, producing the dimethyl titanium complex after eliminating LiCl. This would be interesting as {N-N}2TiMe2 complexes were known to act as olefin polymerisation catalysts. However, due to a lack of pure product being isolated from these reactions and also due to a lack of time this reaction was never attempted.
5.5REACTIONS WITH TETRACHLOROBIS(TETRAHYDROFURAN)ZIRCONIUM

Following the successful characterisation of the titanium guanidinate complex, experiments were undertaken with $[\text{Zr(thf)}_2\text{Cl}_4]$ and diethylidiphenylguanidinate in order to produce the zirconium analogue. It was hoped that reactions would proceed in a similar manner as amidinate complexes of zirconium were known.$^{5-1,5-6,5-15}$

$[\text{Zr(thf)}_2\text{Cl}_4]$ was synthesised by the same method as $[\text{Ti(thf)}_2\text{Cl}_4]$.\(^{(5-13)}\) THF was added dropwise to a solution of $\text{ZrCl}_4$ in dichloromethane and the product was obtained as a colourless crystals after addition of hexane to the reaction mixture. The reactions with diethylidiphenylguanidine were carried out in a similar manner to those for the titanium complex. The guanidine was singly deprotonated with $n\text{BuLi}$ in ether solution then added to a suspension of $[\text{Zr(thf)}_2\text{Cl}_4]$ in ether at $-78^\circ\text{C}$. Unlike the titanium complex, upon addition no distinct colour change was observed and after warming to room temperature the solution had a pale yellow/green appearance. However, a white precipitate had formed in the reaction (presumed to be LiCl and indicative of reaction) and attempts were made to crystallise a reaction product from the mixture.

The first attempt at crystallisation was not successful as problems were encountered while filtering the reaction mixture which led to the solution losing all of its colour. However, when repeated, a yellow/green solution was again obtained and filtration yielded a clear solution. Attempts were made to crystallise this directly from the ether solution but, in similar fashion to the titanium work, no crystalline material was obtained. A final effort was undertaken in which following reaction the solvent was removed to dryness and the residue was extracted with toluene. A very slightly coloured solution was obtained and filtration was required to remove the insoluble precipitate. A clear solution was obtained but unfortunately no crystalline material was recovered.

It was unfortunate that no crystalline product was obtained from these reactions as, apart from being of interest in their own right, these complexes could have had potential as precursors to olefin polymerisation catalysts.$^{(5-13)}$
5.6 EXPERIMENTAL

All solvents were deoxygenated and dried before use by distillation from sodium-benzophenone for ethers and toluene and CaH$_2$ for hexane.

The starting materials and products are air- and moisture sensitive and were handled on a vacuum line using standard inert atmosphere techniques$^{(5-16)}$ under dry, oxygen free nitrogen. Compounds were isolated and characterised with the aid of an nitrogen filled glove box (Saffron) fitted with oxygen and moisture scrubbing columns.

Elemental analysis was performed by sealing samples (approx. 1 mg) under nitrogen in air-tight aluminium boats and determined using a Perkin Elmer 2400 CHN Analyser. Nuclear Magnetic Resonance spectra were recorded on a Gemini 200 MHz and Bruker 250 MHz spectrometers with positive chemical shifts referenced to TMS.

The starting materials [TiCl$_4$(thf)$_2$]$^{(5-13)}$ and [ZrCl$_4$(thf)$_2$]$^{(5-13)}$ were prepared by literature methods. TiCl$_4$ was purchased from Aldrich and used as a standard solution [0.2275 mol dm$^{-3}$] in hexane while [Ti(NMe$_2$)$_4$], kindly provided by Dr. Colin R. Pulham, was used as a standard solution [0.267 mol dm$^{-3}$] in toluene.

5.6.1 REACTIONS OF [Ti(NMe$_2$)$_4$]

All of the reactions of [Ti(NMe$_2$)$_4$] were carried out by the general procedure outlined here. Notable exceptions will be highlighted where appropriate.

The guanidine was weighed into a Schlenk then dried under dynamic vacuum for ten minutes. An atmosphere of nitrogen was introduced and toluene added to dissolve the guanidine with gentle warming as required. To this solution the [Ti(NMe$_2$)$_4$] was added carefully via syringe.

The details of the individual reactions will describe observations, manipulations and measurements made from this point.
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_REACTION WITH TRICYCLOHEXYLGUANIDINE_

Tricyclohexylguanidine (408 mg, 1.33 mmol)

\[[\text{Ti(NMe}_2\text{)}_4]\] (0.67 cm$^3$, 2.5 cm$^3$ of solution, 0.5 eq.)

Toluene (10 cm$^3$).

Upon addition of the \[[\text{Ti(NMe}_2\text{)}_4]\] at room temperature the colour slowly deepened from yellow to orange and over the period of two hours turned scarlet red. The toluene was removed _in vacuo_ to leave a sticky red oil which was taken up in hexane. The solution was filtered through a pad of celite to remove any precipitate and the resulting clear red solution stored at 5°C for a few days. No crystalline material was obtained so the Schlenk was transferred to storage at -30°C. After two days no crystalline material had formed so the volume of hexane was reduced by bubbling nitrogen through the solution. Following a further period of storage at -30°C the concentrated solution did not yield any solid. Continued storage merely resulted in a white precipitate forming while the solution grew paler in colour as a result of decomposition.

_REACTION WITH TRIISOPROPYLGUANIDINE_

Triisopropylguanidine (247 mg, 1.33 mmol)

\[[\text{Ti(NMe}_2\text{)}_4]\] (0.67 cm$^3$, 2.5 cm$^3$ of solution, 0.5 eq.)

Toluene (20 cm$^3$).

Again following addition, the reaction mixture turned from yellow through orange to red while stirring at room temperature. The toluene solvent was removed _in vacuo_ to give a sticky oil which was redissolved in hexane. This solution was filtered through celite and crystallisation was attempted by storage at -30°C. No solid was obtained from this, and no decomposition had occurred either. An aliquot of the solution was dried and a $^1$H NMR measured in CDCl$_3$. The spectrum showed a number of peaks in the ranges $\delta$ 0.9 – 1.4 (CH$_3$ groups of 'Pr) and 3.3 – 3.8 (CH of 'Pr) ppm. The remaining solution was warmed to 50°C although after warming for a short while the solution began to lose colour and a white precipitate formed, indicative of decomposition.
**REACTION WITH TRISOPROPYLGUANIDINE**

Triisopropylguanidine (247 mg, 1.33 mmol)

\[ [\text{Ti(NMe}_2\text{)}_4] (0.67 \text{ cm}^3, 2.5 \text{ cm}^3 \text{ of solution, 0.5 eq.}) \]

Toluene (20 cm³).

The reaction was carried out in a different manner this time in that the \([\text{Ti(NMe}_2\text{)}_4]\) was added to the guanidine which was cooled to -78°C. The mixture was allowed to warm to room temperature and was then refluxed for two hours. The resultant red solution was cooled and the toluene removed to dryness. Sufficient hexane was added to dissolve the residue and the solution was filtered to give a clear, red solution. Storage of this at -30°C did not yield any crystalline material. The solvent was removed \textit{in vacuo} leaving a red solid. Purification was attempted by vacuum sublimation although with gentle warming to \textit{ca.} 50°C only white needles formed on the cold finger. The melting point (57-58°C) confirmed these to be the free ligand. The cold finger was cleaned and the sublimation apparatus reassembled though further heating did not result in any more material subliming. At 150°C the solid in the Schlenk started to decompose, slowly turning black in the process.

**REACTION WITH TRI-p-TOLYLGUANIDINE**

Tri-p-tolyguanidine (438 mg, 1.33 mmol)

\[ [\text{Ti(NMe}_2\text{)}_4] (0.67 \text{ cm}^3, 2.5 \text{ cm}^3 \text{ of solution, 0.5 eq.}) \]

Toluene (20 cm³).

The guanidine was dissolved in toluene (10 cm³) and toluene (10 cm³) was also added to the standard solution of \([\text{Ti(NMe}_2\text{)}_4]\). Both solutions were cooled to -78°C, then the \([\text{Ti(NMe}_2\text{)}_4]\) was added to the guanidine. After addition of one drop a red colour appeared in the reaction mixture and as addition continued the solution colour deepened to red / brown. After addition was complete, the reaction mixture was allowed to warm to room temperature, then was stirred for two hours. The solvent was then removed to dryness and the residual red solid was dissolved in hexane (5 cm³). The red solution obtained was filtered through celite to give a clear solution. Storage of this solution at 5 and -30°C did not yield any crystalline material, the products again proving too soluble in hexane.
**Chapter Five**  
**Reactions with Group IV Metals**

**Reaction with Tri-p-tolylguanidine**

Tri-p-tolylguanidine (219 mg, 0.67 mmol)  
[Ti(NMe₂)₄] (0.67 cm³, 2.5 cm³ of solution, 0.5 eq.)  
Toluene (20 cm³).

In order to maintain the 1:1 stoichiometry the guanidine was added to the [Ti(NMe₂)₄] at -78°C. Upon addition the colour changed from yellow to orange and when allowed to warm to room temperature the reaction solution did not deepen in colour. Attempts to crystallise a product from the reaction by removing the toluene, dissolving the residue in hexane, filtering and cooling did not yield any crystals.

**5.6.2 Reactions of TiCl₄**

**Reaction with Triisopropylguanidine**

Triisopropylguanidine (250 mg, 1.35 mmol)  
nBuLi (1.05 eq., 1.41 mmol, 0.56 cm³ of 2.5 mol dm⁻³ solution in hexane)  
TiCl₄ (0.5 eq., 0.673 mmol, 2.96 cm³ of 0.2275 mol dm⁻³ standard solution)  
THF (20 cm³)

The guanidine was dried under dynamic vacuum then dissolved in THF. The solution was cooled to -78°C, BuLi was added then the solution was warmed to ensure complete reaction. The solution was recooled to -78°C and TiCl₄ was added dropwise. An immediate colour change was observed with the solution turning brown in colour with a white precipitate being produced. The mixture was warmed to room temperature then the solvent was removed *in vacuo*. Attempts to dissolve the dark brown residue failed (even in THF) and the solid was thought to have decomposed.

**Reaction with Triisopropylguanidine**

Triisopropylguanidine (250 mg, 1.35 mmol)  
nBuLi (2.10 eq., 2.82 mmol, 1.13 cm³ of 2.5 mol dm⁻³ solution in hexane)  
TiCl₄ (0.5 eq., 0.673 mmol, 2.96 cm³ of 0.2275 mol dm⁻³ standard solution)
THF (20 cm³)

The methodology described in the previous reaction was used for this reaction. Dropwise addition of the TiCl₄ to the dilithioguanidinate again gave rise to an instant colour change. As addition continued the colour changed from colourless through yellow to brown during which time a pale precipitate formed. After warming to room temperature, filtration through celite yielded a deep red coloured solution. The solvent was removed in vacuo and a ¹H NMR (200 MHz, CDCl₃) of the oily residue was obtained. The spectrum showed two distinct, though ill-defined, groups of peaks at δ 1.0 – 1.4 ppm (CH₃ of the 'Pr groups) and δ 3.3 – 3.7 ppm (CH of the 'Pr groups). The oil was dissolved in the minimum volume of hexane (ca. 5 cm³) and attempts were made to crystallise the product. After no crystals had been obtained the solvent was removed to dryness and purification attempted by vacuum sublimation. Warming of the solid under dynamic vacuum resulted in the collection of white needles before the solid started to decompose.

**REACTION WITH TRIISOPROPYLGUANIDINE IN HEXANE**

Trisisopropylguanidine (300 mg, 1.62 mmol)

nBuLi (2 eq., 3.23 mmol, 1.29 cm³ of 2.5 mol dm⁻³ solution in hexane)

TiCl₄ (0.5 eq., 0.808 mmol, 3.55 cm³ of 0.2275 mol dm⁻³ standard solution)

Hexane (100 cm³)

Lithiation of the guanidine in hexane proceeded smoothly at -78°C. Upon warming to room temperature a white precipitate formed which persisted. The suspension was cooled to -78°C and TiCl₄ added dropwise. An immediate colour change to red was observed and with addition of TiCl₄ it was difficult to determine whether the white precipitate was being consumed in the reaction. After addition was complete, the solution was deep red with a pale precipitate. Filtration through celite yielded a clear solution, then the solvent volume was reduced to a minimum. Storage at 5°C followed by -30°C did not yield any solid material.
5.6.3 REACTIONS OF [TiCl₄(thf)₂] WITH TRISUBSTITUTED GUANIDINES

**SYNTHESIS OF [TiCl₄(thf)₂]**

[TiCl₄(thf)₂] was synthesised following the method of Manzer.⁵⁻¹³

TiCl₄ (5.00 g, 26.3 mmol) dissolved in DCM (50 cm³), to which THF (8.6 cm³, 0.10 mol) was added dropwise with stirring. A violent reaction occurred in which the solution rapidly changed colour and a yellow solid was produced. During THF addition, the solid started to redissolve though after addition was complete the solid precipitated once more. Hexane (50 cm³) was added to the reaction mixture and it was stored at -30°C overnight. A bright yellow solid was obtained and this was collected by filtration and washed with hexane (20 cm³) with a final yield of 7.95 g (90%).

**REACTION WITH GUANIDINES**

The reactions of [TiCl₄(thf)₂] with guanidines were undertaken using the same methodology. The guanidine was dried under dynamic vacuum then dissolved in diethyl ether. This solution was cooled to -78°C then cannulated into a suspension of [TiCl₄(thf)₂], also in ether. Following reaction, crystallisation was attempted by filtering the reaction solution then storing the solution at 5 and -30°C. Details of the individual reactions follow.

**WITH TRISOPROPYLGUANIDINE**

Triisopropylguanidine (1.79 mmol, 333 mg)

nBuLi (1.79 mmol, 0.72 cm³ of 2.5 mol dm⁻³ solution)

[TiCl₄(thf)₂] (0.5 eq., 0.90 mmol, 300 mg)

Ether (25 cm³)

Upon addition the colour changed from yellow to red and [TiCl₄(thf)₂] was consumed by the reaction. Following warming to room temperature, the reaction mixture was filtered and the solvent removed to dryness. ¹H NMR (200 MHz, CDCl₃) of the residual solid had peaks from the ³Pr functions at δ 1.24 (d, (CH₃)₂CH) and 3.75 (q, (CH₃)₂CH) ppm. The residual solid was insoluble in hexane (20 cm³)
though the majority was soluble in ether (20 cm$^3$). Filtration of this solution yielded a clear, red solution though all attempts to crystallise the product failed. No further spectroscopic data was obtained.

*WITH TRICYCLOHEXYLGUANIDINE*

Tricyclohexylguanidine (1.20 mmol, 366 mg)
$n$BuLi (1.20 mmol, 0.48 cm$^3$ of 2.5 mol dm$^{-3}$ solution)
[TiCl$_4$(thf)$_2$] (0.5 eq., 0.60 mmol, 200 mg)
Ether (20 cm$^3$)

Addition of the guanidine resulted in formation of red solution. The solvent volume was reduced to ca. 5 cm$^3$ before filtration through a pad of celite. Following filtration a red solution was obtained though this still contained white precipitate. Filtration was repeated though a precipitate again persisted. No attempts at crystallisation were made with this solution and no spectroscopic data was obtained.

*WITH TRIPHENYLGUANIDINE*

Triphenylguanidine (2.16 mmol, 620 mg)
$n$BuLi (2.16 mmol, 0.86 cm$^3$ of 2.5 mol dm$^{-3}$ solution)
[TiCl$_4$(thf)$_2$] (0.5 eq., 1.08 mmol, 360 mg)
Ether (25 cm$^3$)

Upon addition the solution changed colour to red. Cannula filtration was attempted as was filtration through celite though a white precipitate persisted in the reaction mixture. Upon further filtration through celite, a clear solution was obtained and storage of this solution at -30°C did not yield any solid material. Hexane (5 cm$^3$) was added dropwise until a precipitate was observed in the Schlenk. Addition of some ether with gentle warming of the mixture did not redissolve the precipitate and filtration through celite resulted in the solution losing colour.
5.6.4 **REACTIONS OF [TiCl\textsubscript{4}(thf)]\textsuperscript{−} WITH TETRASUBSTITUTED GUANIDINE**

**SYNTHESIS OF [Ti{(PhN)\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}Cl\textsubscript{2}] 51**

Diethylidiphenylguanidine (705 mg, 2.64 mmol) was dissolved in diethyl ether (20 cm\textsuperscript{3}) and cooled to -78°C. nBuLi (2.64 mmol, 1.05 cm\textsuperscript{3} of 2.5 M solution) was added and the mixture stirred for 10 minutes then allowed to warm to room temperature. This solution was recooled to -78°C, then added to a suspension of [TiCl\textsubscript{4}(thf)]\textsuperscript{−} in diethyl ether (20 cm\textsuperscript{3}) at -78°C. An instant colour change was observed, with a bright red solution forming as reaction proceeded. The mixture was warmed to room temperature and stirred for 18 hours. The resulting red solution was dried *in vacuo* leaving a red solid which was dissolved in toluene (10 cm\textsuperscript{3}). Filtration of this solution through celite yielded a clear red solution which, upon storage at -30°C, produced red needles. These were found to be of insufficient quality for X-ray diffraction. The solution was re-filtered through celite and the resulting solution was stored at 5°C. After a few weeks the solution afforded a crop of red needles 51, ca. 20%; \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}) : \(\delta\) 0.84 (t, \(J = 7.2\) Hz, 12H, CH\textsubscript{2}-CH\textsubscript{3}), 2.64 (q, \(J = 7.2\) Hz, 8H, CH\textsubscript{2}-CH\textsubscript{3}), 6.93 - 7.27 (cm, 20H, ArH) ppm; \textsuperscript{13}C NMR (62.896 MHz, CDCl\textsubscript{3}) : \(\delta\) 12.84 (CH\textsubscript{2}-CH\textsubscript{3}), 42.20 (CH\textsubscript{2}-CH\textsubscript{3}), 121.70 - 125.16 (ArC) ppm; CHN : Found C 59.91, H 5.79, N 13.29; C\textsubscript{34}H\textsubscript{40}N\textsubscript{6}Cl\textsubscript{2}Ti requires C 62.28, H 6.19, N 12.90.

**Crystal Data for [Ti{(PhN)\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}Cl\textsubscript{2}] 51.**

Data were collected using Mo-K\textsubscript{α} radiation on an oil coated\textsuperscript{(5-17)} red needle of dimensions 0.58 x 0.16 x 0.12 mm on a Stoe Stadi4 diffractometer in the range 6\(\leq\theta\leq\)50° using the \(\omega-\phi\) method. Of a total of 7216 reflections collected, 3675 (\(R_{int} = 0.0639\)) were independent. The structure was solved by direct methods (SIR 92)\textsuperscript{(5-18)} and refined using SHELXL-97. Hydrogen atoms were geometrically fixed and allowed to ride. The toluene molecule in the unit cell was disordered. The final difference-map extrema were 0.866 and -0.765 e Å\textsuperscript{−3} with a final \(R\) of 0.0688 for 219 parameters.
5.6.5 REACTIONS OF [ZrCl₄(thf)]₂ WITH TETRASUBSTITUTED GUANIDINES

SYNTHESIS OF [ZrCl₄(thf)]₂

This followed the procedure described by Manzer.⁵⁻¹³

To a suspension of ZrCl₄ (1.51 g, 6.49 mmol) in DCM (20 cm³), THF (1.05 cm³, 13.00 mmol) was added dropwise. An exothermic reaction takes place with ZrCl₄ being slowly consumed. After stirring for two hours the solution was filtered through celite and hexane (30 cm³) was added to the colourless filtrate causing a white precipitate to form. This was redissolved with stirring and the solution was stored at -30°C. A crop of colourless crystals were obtained, which were collected by filtration, washed with hexane and dried (1.00 g, 40%).

REACTION OF [ZrCl₄(thf)]₂ WITH DIETHYLDIPHENYLGUANIDINE

A typical reaction of this type is detailed as follows.

Diethylidiphenylguanidine (266 mg, 0.997 mmol) was dissolved in diethyl ether (15 cm³) and the solution cooled to -78°C. To this, nBuLi (0.997 mmol, 0.39 cm³ of 2.5 M solution) was added and the solution stirred for 10 minutes before being allowed to warm to room temperature. The solution was re-cooled to -78°C then transferred via cannula to a suspension of [ZrCl₄(thf)]₂ (188 mg, 0.498 mmol, 0.5 eq.)
in diethyl ether (15 cm³). No colour change was observed after addition, although the 
[ZrCl₄(thf)₂] did appear to be taken into solution. The mixture was allowed to warm to room temperature and the solution turned pale green. After stirring for 18 hours, filtration through celite yielded a clear pale green solution. The solvent volume was reduced to a minimum and storage at -30°C did not yield any crystalline material.

In a repeat of this reaction, after filtration the solvent was removed to dryness. The residue was dissolved in toluene, filtered and stored at 5 then -30°C however, no crystalline material was obtained.
5.7 REFERENCES

Chapter Six

REATIONS WITH MAIN GROUP METALS

The reactions of substituted guanidines with the metallating agents antimony tris(dimethylamide) \([\text{Sb(NMe}_2\text{)}_3]\), tin bis(dimethylamide) \([\text{Sn(NMe}_2\text{)}_2]\) and dicyclopentadienyltin \([\text{Cp}_2\text{Sn}]\) were studied in collaboration with Dominic S. Wright during a visit to the University of Cambridge.

\([\text{M(NMe}_2\text{)}_3]\) \((M = \text{Sb, Sn})\) are known to be highly reactive reagents which readily deprotonate compounds evolving dimethylamine \((\text{HNMe}_2)\) to form complexes with the deprotonated compound ligated to the metal. This is very desirable as with the by-product being a gas at room temperature only the product(s) remain in solution. This is clearly advantageous as the relative amount of product obtained is increased which serves to aid crystallisation while lessening the likelihood of crystallising any by-products.

The reaction of a range of tri- and tetrastubstituted guanidines with \([\text{Sb(NMe}_2\text{)}_3]\) were studied in 1:1 and 2:1 (ligand to metal) molar ratios. Reactions with primary and lithiated primary amines had previously been reported\(^{263}\) though the reaction of \([\text{Sb(NMe}_2\text{)}_3]\) with a guanidine was previously unknown.

Investigative reactions of tin bis(dimethylamide) \([\text{Sn(NMe}_2\text{)}_2]\) and dicyclopentadienyltin \([\text{Cp}_2\text{Sn}]\) with guanidines were also carried out. \([\text{Sn(NMe}_2\text{)}_2]\) was known to react with amines, in a similar manner to the analogous antimony complex, to form \(\text{Sn}_4\text{N}_4\) cubanes.\(^{6-4}\) Nucleophilic addition and substitution reactions of \([\text{Cp}_2\text{Sn}]\) with anionic nucleophiles have also been reported with a range of complexes and their structures characterised.\(^{6-5,6-6,6-7}\) Whether substitution or addition occurs is generally dependant on the relative nucleophilicity of the anions concerned.

It was anticipated that guanidines would react with these main group reagents to form novel complexes increasing the small number of main group guanidinate complexes already known.
6.1 ANTIMONY TRIS(DIMETHYLAMIDE)

[Sb(NMe₂)₃] is synthesised in the reaction of antimony trichloride with three equivalents of lithium dimethylamide. It is obtained, by vacuum distillation, as a colourless liquid which rapidly hydrolysates to form antimony oxide [Sb₂O₃]. Due to its moisture sensitivity, [Sb(NMe₂)₃] was most conveniently stored and used as a standard solution in toluene and, unless otherwise stated, all of the reactions reported here were performed using toluene as solvent.

A further feature of the air and water sensitivity of the starting material and the anticipated sensitivity of the products, is that purification of products could only be attempted by crystallisation or sublimation. For this reason and also because my time in Cambridge was limited, the initial aim of all reactions was to isolate crystals suitable for X-ray study. If this was achieved the reaction would then be repeated in order to obtain an additional sample of product suitable for analysis leaving the crystalline sample for X-ray study if desired.

6.1.1 Equimolar Reaction of [Sb(NMe₂)₃] with Trisubstituted Guanidines

[Sb(NMe₂)₃] had previously been used in the synthesis of group 15 heteroatom complexes by its reaction with both lithiated and non-lithiated primary amines to form a series of polyamidoantimonate complexes. With trisubstituted guanidine molecules having two secondary amine functions it is possible for guanidines to be singly or doubly deprotonated in their reaction with [Sb(NMe₂)₃]. As a consequence of this, in the reaction with one equivalent of [Sb(NMe₂)₃] there is clearly a variety of products which could form due to the non-regular stoichiometry of the reactive species, i.e. one mole of [Sb(NMe₂)₃] is able to deprotonate one and a half moles of guanidine. Hence, in a mononuclear complex one possible outcome of this would be for the metal centre to be coordinated by a dianionic guanidinate and a monoanionic ligand, balancing the antimony's +3 oxidation state. The dianionic guanidinate was expected to coordinate to the metal as
a bidentate ligand and it was reasoned that the monoanionic ligand could be residual dimethylamide, which had been previously observed,\(^{(6-10)}\) or a monoanionic guanidine. This however, would result in the antimony being only three coordinate so some degree of oligomerisation could not be ruled out. Furthermore, due to the flexibility of the guanidinate ligands, products containing more metal centres bridged by mono- and dianionic guanidinates were as readily perceivable, highlighting the need for X-ray crystal structure determinations in order to fully elucidate the structure of the product obtained.

6.1.1.1 REACTION WITH TRI-p-TOLYLGUANIDINE

Addition of \([\text{Sb(NMe}_2]_3\) to a toluene solution of tri-p-tolylguanidine immediately produced an orange solution from which a sticky oil was obtained. Following dissolution and filtration of the oil, crystallisation was attempted by concentration and slow cooling of toluene/hexane mixtures though the product either formed an oil or precipitated to yield a powder. In an attempt to slow precipitation and also prevent a thick oil forming, THF was added and the solution was allowed to cool slowly in the fridge. Initially a small amount of oil formed and this was left in the fridge to see if it would crystallise. After one week small, yellow crystals suitable for X-ray study were formed. An X-ray crystal structure determination of this product was undertaken although due to a problem with the cryostream the crystal decomposed when mounted in the diffractometer. Unfortunately, decomposition of the remaining product had also occurred and all the product was lost.

The reaction was repeated and again a bright orange solution was obtained upon addition. Crystallisations were attempted as before but no crystals of suitable quality were obtained.

6.1.1.2 REACTION WITH TRIS-\(\alpha\)-METHYLBENZYLGUANIDINE

Reaction of \([\text{Sb(NMe}_2]_3\) with the chiral tris-\(\alpha\)-methylbenzylguanidine in toluene solution proceeded very slowly at room temperature. After 48 hours stirring
no colour change had been observed and the IR spectrum of the reaction mixture showed no change for the C＝N stretch (1638 cm⁻¹). The mixture was warmed to 50°C for four hours then refluxed for one hour. The solution turned yellow though some decomposition also occurred. Following filtration and concentration an orange oil was obtained from which no crystals formed.

6.1.1.3 Reaction with Triisopropylguanidine

This reaction was also attempted with triisopropylguanidine which upon addition of [Sb(NMe₂)₃] showed a gradual colour change from colourless to yellow. Gentle warming of the solution over a period of two hours resulted in a yellow solution and, after stirring for a further hour, the solvent was removed in vacuo. The residue was dissolved in warm hexane though some precipitate had formed through decomposition. The precipitate was allowed to settle then the solution was filtered through a celite pad to give a bright, clear, yellow solution. Concentration of the solution resulted in precipitation of the product which completely redissolved upon warming in a water bath. Gradual cooling of this solution in the water bath, aided by insulation of the Schlenk, provided highly air-sensitive, X-ray quality crystals in a 10% yield.

A low temperature X-ray crystallographic study of an oil coated crystal showed the crystal to be chiral with space group P3₁2₁ or P3₂2₁. The product, [Sb{(Pr'N)₂CNHPr'}{(Pr'N)₂CNPr'}] 61, consists of a four-coordinate antimony ion chelated by two anionic guanidinate ligands (Fig. 6.1).

![Figure 6.1. Isolated product of the reaction between [Sb(NMe₂)₃] and triisopropylguanidine.](image)
Formally the guanidinates must be monoanionic and dianionic in order to balance the +3 charge of the antimony(III) centre though the ligands were indistinguishable in the crystal structure. This was confirmed by $^1$H NMR spectroscopy of the isolated product in which there are five independent isopropyl groups in the ratio 1:1:1:1:2. This is consistent with free rotation around the uncoordinated C-NHPR\(^t\) bond of the monoanionic ligand while the C=NPR\(^t\) bond of the dianionic ligand remains static.

In the crystal structure the indistinguishability of the ligands is primarily due to the involvement of the N-H proton on the monodeprotonated guanidine in hydrogen bonding. To overcome this, these N-H protons were placed in calculated positions and were allowed to ride between their respective nitrogen atoms with a site occupancy of 0.5.

The formation of 61, which retains an N-H hydrogen despite the presence of sufficient metallating agent in the reaction mixture to remove all such protons, may be as a result of preferential crystallisation of the hydrogen-bonded partially metallated species and explain its low yield.

Within the unit cell there are two independent, but chemically equivalent, molecules differing only in the conformations of their isopropyl groups and in their bond lengths and angles. One molecule lies on a twofold rotational axis which relates the two ligands (Fig. 6.2) while the other lacks this axis. Discussion of the structure of this complex will be limited to the molecule containing the symmetry axis.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(1)-N(11)</td>
<td>2.227(6)</td>
<td>62.0(2)</td>
</tr>
<tr>
<td>Sb(1)-N(13)</td>
<td>2.069(6)</td>
<td>140.3(3)</td>
</tr>
<tr>
<td>C(10)-N(11)</td>
<td>1.372(10)</td>
<td>104.5(3)</td>
</tr>
<tr>
<td>C(10)-N(12)</td>
<td>1.311(11)</td>
<td>93.1(2)</td>
</tr>
<tr>
<td>C(10)-N(13)</td>
<td>1.342(10)</td>
<td></td>
</tr>
<tr>
<td>N(12)…N(12a)</td>
<td>3.148(12)</td>
<td>160</td>
</tr>
</tbody>
</table>

*Table 6.1. Selected bond lengths (Å) and angles (°) for 61.*
Figure 6.2. Molecular structure of 61. Isopropyl CH₃ groups have been omitted for clarity.
Along with the guanidinate ligands the antimony centre also has a residual lone pair and so the molecular structure of 61 is consistent with the ten-electron count of the antimony centre. Though on first inspection it would be anticipated that the complex exhibits square pyramidal geometry, it can actually best be described as a heavily distorted trigonal-bipyramidal N₄Sb molecule in which the lone pair occupies the fifth (equatorial) coordination site. Evidence of this arises upon inspection of the bond lengths and angles at the antimony centre. In both independent molecules the SbIII centre is asymmetrically coordinated by the two guanidinate ligands [e.g. Sb(1)-N(11) 2.227(6) Å, Sb(1)-N(13) 2.069(6) Å]. This is consistent with the description of the structure as a trigonal bipyramid since in this geometry each ligand would be coordinated to an axial and equatorial position as opposed to a square pyramidal system in which the coordinate bonds would be symmetrical. The heavily distorted nature of the complex can be appreciated by consideration of the chelating N-Sb-N angle at the metal. For a regular trigonal bipyramid this would be 90° though in 61 it is far more acute [N(11)-Sb(1)-N(13) 62.0(2)°] as a consequence of the rigid geometric constraints imposed by the guanidine ligand. The result of this is that the N-Sb-N angle from the axial N centres is distorted from 180° [N(11)-Sb(1)-N(11a) 140.3(3)°] and that for the equatorial N centres is distorted from 120° [N(13)-Sb(1)-N(13a) 104.5(3)°] as required for ideal trigonal-bipyramidal geometry.

The distorted trigonal-bipyramidal geometry of the antimony centres in 61 is very similar to the environment of the central metal atom in the [(Me₂N)Sb(NC₆H₁₁)₂]₂Sb monoanion, the only other previously characterised SbIII centre surrounded by four nitrogen ligands.(64) The major difference, in terms of geometrical parameters, between these two systems is that in 61 the guanidinate ligands chelate the antimony so any restrictions in the ligand may directly govern the geometry at the antimony centre. This is not the case for [(Me₂N)₂Sb(NC₆H₁₁)₂]²⁻ as the ligands are all monohaptic with respect to the central metal atom though their polyhapticity within the molecular framework may have some bearing on the geometry observed at the central metal centre.

The hydrogen bonding present in the solid state occurs between the uncoordinated NPr' groups of ligands on adjacent molecules. This results in the
formation of long hydrogen bonded $\text{H}\ldots\text{L-Sb-L-H}\ldots\text{L-Sb-L-H}\ldots\text{L}$ chains of molecules (Fig. 6.3).

![Diagram of hydrogen bonding network in 61.](image)

**Figure 6.3. Hydrogen bonding network in 61.**

The hydrogen bonds have a $\text{N}\ldots\text{N}$ separation of 3.184(12) Å and placement of the hydrogen atoms in their calculated positions in the crystal structure gives $\text{N-H}\ldots\text{N}$ angles of $160^\circ$. As a consequence of the alignment of these groups, which is dictated directly by the distorted trigonal-bipyramidal geometry present in 61, the chains of molecules form left-handed helices through the crystal studied with three molecules of 61 per 360° turn (Fig. 6.4). As the guanidinate ligands are achiral it is probable that other crystals have the opposite chirality and form right handed helices.

![Diagram of hydrogen bonded chain of 64.](image)

**Figure 6.4. Hydrogen bonded chain of 64. Side view of a section of the helix shell and axial view though the central cavity of the helix.**
The formation of helical structures is very rare for transition and main group metal compounds. The most common systems in which helices have been identified are polymeric phosphido and amido lithium complexes. These polymers are formed by the association of solvated lithium cations and diorgano-phosphides or amides. The phosphide complexes form zig-zag -Li-P-Li-P-Li-P- chains, the structure of which are determined by the geometry at the lithium and phosphorous centres. The chains are generally only two-dimensional although introduction of steric strain into the system will cause the chains to twist. For example, in [Li(Et₂O)PPh₂]ₘ the chains are flat though for [Li(thf)P(C₆H₁₁)₂]ₘ increased steric strain causes the chains to twist and form helices. In the X-ray crystal structure of [Li(thf)₂PH(Mes)] (Mes = mesitylene) the two enantiomeric helical forms were identified in the unit cell. The crystal structure of lithium diisopropylamide also revealed that the complex formed an infinite helical arrangement composed of four N-Li-N units per turn.

These helices are formed from chains of molecules which are all bonded together however, the heterometallic cluster [Ru₃(CO)₆(μ-SnR₂)(μ-SnR'₂)₂] (where R = CH(SiMe₃)₂ and R' = 2,4,6-triisopropylphenyl) exists as a discreet molecule and only forms helices when packing in the solid state. This occurs as a result of there being a twist at the diaryltin centre which is not found at the dialkyl centre.

The helical structure of 61, arising from the inherent distortion of the complex, is different again as the discreet molecular units are associated by hydrogen bonds. This phenomenon has very rarely been observed in metal complexes and the hydrogen-bonded association in 61 is, to my knowledge, unprecedented for any metallo-organic complex.
6.1.2 Reaction of [Sb(NMe₂)₃] with Two Equivalents of Trisubstituted Guanidines

The 2:1 molar reactions (guanidine : metal) of trisubstituted guanidines with [Sb(NMe₂)₃] were expected to yield complexes containing mono- or dianionic guanidinates acting as chelating ligands. As a result of having two guanidinate ligands per metal, it was expected that the product of these reactions would be monomeric, the coordination sphere of the antimony taken up by four ligating nitrogens. Indeed, it was for this stoichiometry that a bis-chelate complex containing mono- and dianionic ligands was anticipated (rather than for the equimolar reaction as detailed previously!!).

6.1.2.1 Reaction with Tri-p-Tolylguanidine

The addition of [Sb(NMe₂)₃] to a solution of the guanidine in toluene immediately produced a bright yellow / orange colour. After stirring for an hour at room temperature the reaction mixture was filtered to remove decomposition products. Upon reduction of the volume of toluene to a few cm³, a fluffy, yellow precipitate crashed out of solution. Rewarming of the solution dissolved all of the precipitate though air cooling of the solution yielded only precipitate. Attempts were made to crystallise the product by cooling the solution slowly in an oil bath; adding extra toluene and THF but on each occasion only a fine, yellow precipitate was obtained.

6.1.2.2 Reaction with Tricyclohexylguanidine

After addition of [Sb(NMe₂)₃] to a solution of tricyclohexylguanidine a colour change from colourless to pale yellow was observed while stirring at room temperature for two hours. The reaction mixture was filtered to remove decomposition then the solvent volume was reduced to a few cm³. Addition of hexane did not cause any precipitation so the solvent was removed to dryness. The sticky, white solid that remained was readily soluble in hexane and cooling of a concentrated solution yielded
a white powder. After isolation, infra red spectroscopy confirmed this solid to be free, unreacted guanidine (νC=N 1640 cm⁻¹). The remaining filtrate was recooled and a further crop of the powder was obtained, which was also free guanidine. The combined weight of the two crops of guanidine revealed that all had been recovered and no reaction had occurred.

The reaction was repeated and heated to reflux for twenty-four hours during which time no colour change was observed. After cooling and removal of the solvent a white solid remained which was found, by infra red, to be free guanidine.

6.1.3 Reaction of Tetrasubstituted Guanidines with \([\text{Sb(NMe}_2\text{)}_3]\)

The reaction of the tetrasubstituted diethyl-diphenylguanidine with \([\text{Sb(NMe}_2\text{)}_3]\) was attempted in both 1:1 and 2:1 molar ratios (guanidine : metal). With this ligand having only one amino proton, the guanidine can only undergo a single deprotonation and it was hoped that this restriction would result in different products being obtained than for the trisubstituted guanidines.

In equimolar stoichiometry no reaction was observed at room temperature and the only solid isolated from the reaction was free guanidine ligand. When repeated the reaction mixture was refluxed for twenty-four hours which gave rise to a yellow solution although grey precipitate also formed through decomposition. Filtration yielded a clear yellow solution though all attempts to obtain crystals failed.

The reaction of two equivalents of guanidine with \([\text{Sb(NMe}_2\text{)}_3]\) was only carried out at room temperature. Initially a pale yellow colour was observed in the reaction mixture though precipitation with hexane produced a white solid which was confirmed as free guanidine by IR spectroscopy. The guanidine was isolated by filtration and was equal in weight to the amount added confirming that no reaction had occurred.
6.1.4 Reactivity of Guanidines with \([\text{Sb(NMe}_2\text{)}_3]\)

A factor which became clear while studying these reactions was the difference in the rate of reaction, which seemed dependent on the nature of the substituents on the guanidine. A trend was observed in which alkyl guanidines reacted slowly (or not at all) at room temperature whereas, in comparison, the aryl guanidines reacted very quickly. This observation can be rationalised by stepwise consideration of the reactions taking place.

The first step in the reaction will involve a dimethylamide ligand acting as a base to deprotonate the guanidine molecule. One equivalent of dimethylamine gas will be evolved as a result of this, leaving the guanidinate coordinated to the antimony centre. Once coordinated the second deprotonation of the guanidine will occur more rapidly than the first due to the dianion being more stable than the monoanion (see page 3) and also because of the closer proximity of the guanidine to the metal centre (c.f. the chelate effect). Therefore, from this analysis it becomes clear that the rate determining step in the reaction is the first deprotonation of the guanidine.

In order for this step to occur the dimethylamide ligand must be sufficiently basic to deprotonate the guanidine molecule. However, in these reactions the dimethylamide ligand is common and the only variable factor is the substituents on the guanidine. Hence, it is the acidity of the amino protons on the guanidines which determines the rate of reaction.

Following deprotonation of the guanidine a negative charge remains on the molecule. When an aryl substituent is on the guanidine this charge can be delocalised over the ring resulting in an energetically more favourable situation than for an alkyl substituent which cannot facilitate dissipation of the charge. Consideration of the pk\(_A\) values of amines with alkyl and aryl substituents confirms this, e.g. the pk\(_A\) of aniline is 4.60 while the pk\(_A\) for cyclohexylamine is 10.63.\(^{(6-15)}\) Hence, aniline is considerably more acidic than cyclohexylamine.

Extrapolation of this suggests that the amine protons of the aryl derivatives are more acidic than their equivalent alkyl guanidines and hence, why aryl substituted guanidines react faster than alkyl guanidines.
6.2 Tin Bis(dimethylamide)

\[ \text{[Sn(NMe}_2\text{)]}_2 \] is obtained as a pale yellow solid from the reaction of tin(II) chloride with lithium dimethylamide. Previous work with this reagent by Wright et al found \([\text{Sn(NMe}_2\text{)]}_2\) to doubly deprotonate primary amines \((\text{RNH}_2)\) and these "[Sn(NR)]" units were found to oligomerise and form \(\text{Sn}_4\text{N}_4\) cubanes in the solid state. The structure of \([\text{Sn(NC}_6\text{H}_{11})]_4\) was found to be regular with all Sn-N bonds crystallographically equivalent \([2.195(4)-2.205(4) \text{ Å}]\) and average angles at the tin and nitrogen atoms are uniform \([80.8° \text{ and } 98.5° \text{ respectively}]\). Although guanidines contain two secondary amine functions and not primary amines it was still expected that \([\text{Sn(NMe}_2\text{)]}_2\) would doubly deprotonate a guanidine to yield a complex with the guanidinate dianion chelating to, or more likely, bridging tin centres (Fig. 6.5).

However, one disadvantage of \([\text{Sn(NMe}_2\text{)]}_2\) is that it is only reasonably stable at room temperature and after storage under argon for two weeks its solubility in organic solvents is somewhat reduced. The \([\text{Sn(NMe}_2\text{)]}_2\) used in these reactions was a few weeks old and showed only limited solubility in toluene / THF mixtures. However, synthesis of a fresh batch would have been overly time consuming so it was decided to undertake reactions and assess if any reaction had occurred.

The equimolar reaction of \([\text{Sn(NMe}_2\text{)]}_2\) with triisopropylguanidine in toluene / THF (10:1) did not show a colour change after twenty-four hours stirring at room temperature. Subsequent warming to 80°C for 5 hours merely caused precipitation of a grey solid (presumed to be tin metal). The mixture was filtered to give a clear, pale yellow solution which upon evaporation yielded a small amount of a dark yellow oil. No attempts were made to crystallise this product.

A similar reaction was attempted with tri-\(p\)-tolylguanidine though no reaction was observed at room temperature. The mixture was then refluxed for five hours during which time no colour change was observed. Filtration of the reaction mixture resulted in a clear yellow solution which was dried in vacuo to give a pale yellow
powder. Attempts to crystallise the powder from THF / hexane mixtures were unsuccessful, leading to precipitation of a grey solid due to decomposition.

It is very difficult to draw any conclusions from the work with \([\text{Sn(NM}_{2}\text{e}_{2})_{2}]\) as although reactions seemed to have taken place, the fact that the starting material had decomposed to some extent obviously had an effect on the outcome of reactions. This was unfortunate as a comparison between the products formed by the reaction with secondary amines and the previously studied primary amines would have been of interest. Also of interest would be to find out what effect of having more than one ligating atom on the ligand would have on the structure of product.
6.3 DICYCLOPENTADIENYLTIN

The reaction of Cp₂Sn\(^{(6-17)}\) with nucleophiles had previously been studied as reviewed by Jutzi.\(^{(6-18)}\) More recently however, Wright and co-workers have reported a wide variety of nucleophilic reactions with group 15 donors, including addition and substitution. One example of this work is the formation of the mixed ligand triorganostannate formed in the reaction of Cp₂Sn, LiN(SiMe₃)₂ and pmdeta (1:1:1).\(^{(6-5)}\) The X-ray crystal structure revealed the product to be (Cp)(Me₃Si)₂NSn(m-Cp)Li•pmdeta, formed by nucleophilic addition of LiN(SiMe₃)₂ to Cp₂Sn.

An example of nucleophilic substitution of Cp₂Sn, in which both the Cp ligands are substituted, was recently published.\(^{(6-6)}\) In this case reaction of Cp₂Sn with the monolithiated primary amine, RNHLi (R = 2-MeOC₆H₄), results in the formation of the tris(amido)stannate [(RNH)Sn(μ-NHR)₂Li]₂THF.

Of more direct interest to this thesis is the equimolar reaction of Cp₂Sn with lithio-tetramethylguanidine, also reported by Wright \textit{et al.}\(^{(6-7)}\) Imino anions are strong nucleophiles and in this case the monoanionic guanidine monosubstitutes a Cp ligand to form the complex [CpSnN=C(NMe₂)₂] which forms a centrosymmetric dimer \([\eta^3\cdot\text{Cp}]\text{Sn}\{\mu_2\cdot\text{N}=\text{C}(\text{NMe}_2)\}_2\] in the solid state. The dimer contains a Sn₂N₂ ring with the guanidinates bridging the tin centres through their imino nitrogens.

Consideration of these reactions led us to believe that reaction of Cp₂Sn with dilithiated guanidines would result in the substitution of one or two Cp ligands (formation of LiCp) yielding tin guanidinate complexes. Also, in the examples described above the products are generally found to have tin centres with a coordination number of three. This therefore requires there to be three coordinating (lithiated) sites per tin atom in the reaction stoichiometry. To provide this, the reactions were carried out in 3:2 molar ratio (dilithiated guanidine : Sn). One anticipated product from these reactions was a dinuclear species bridged by two guanidinate ligands with the guanidinates acting as tridentate ligands binding through two of their nitrogen atoms (Fig. 6.6).
Dilithiation of tri-p-tolylguanidine in THF produced an insoluble white solid upon warming to room temperature. Dropwise addition of a Cp₂Sn solution in THF to this mixture instantly resulted in a yellowing of the solution and the white precipitate was gradually consumed in the reaction. After the addition was completed, the solution was a very deep orange colour and no precipitate persisted. The reaction mixture was gently warmed to ensure the reaction had gone to completion. This caused the precipitation of some solid which surprisingly redissolved upon return to room temperature. The inverse solubility of the reaction mixture was repeatable, warming of the solution producing precipitate which redissolved on cooling. Attempts at crystallisation were undertaken by reducing the solvent volume until some precipitate formed. Cooling of this dissolved the solid and the clear solution was allowed to warm slowly. However, these attempts were unsuccessful and only powdery precipitate was obtained.

The analogous reaction was carried out using tricyclohexylguanidine and a similar colour change from yellow to orange was observed though a white precipitate was also produced. The mixture was filtered to give a clear orange solution from which no crystals were obtained.

Similarly, the reaction with the dilithiated tris-α-methylbenzylguanidine changed colour from yellow to orange though the change was not as marked as in the previous reactions. The solution was filtered to remove the small amount of precipitate which had formed during the reaction and to the clear, orange solution ether was added dropwise until precipitation occurred. Warming of the solution redissolved the precipitate though on standing at room temperature or cooling no crystals were obtained.

These reactions of Cp₂Sn with lithiated guanidines showed a good deal of promise with a consistent colour change upon reaction observed for each of the guanidines. However, due to my stay in Cambridge being limited I was not able to explore this area to any greater depth.
6.4 EXPERIMENTAL

All solvents were deoxygenated and dried before use by distillation from sodium-benzophenone for ethers and toluene and CaH₂ for hexane.

The starting materials and products are air- and moisture sensitive and were handled on a vacuum line using standard inert atmosphere techniques under dry, oxygen free argon. Compounds were isolated and characterised with the aid of an argon-filled glove box (Miller-Howe) fitted with oxygen- and water-recirculation systems.

Infrared spectra were recorded on a Perkin Elmer 2400 spectrophotometer. Elemental Analysis were performed by firstly sealing samples under argon in air-tight aluminium boats (1-2 mg) and determined using a Perkin Elmer 240 CHN Elemental Analyser. Nuclear Magnetic Resonance spectra were recorded on a Bruker WH 250 MHz spectrometer with positive chemical shifts referenced to TMS.

The starting materials [Sb(NMe₂)₃], [Sn(NMe₂)₂] and Cp₂Sn were prepared in the manner described in the literature. [Sb(NMe₂)₃] was used as a standard solution [1.93 mol dm⁻³] in toluene as was Cp₂Sn [2.25 mol dm⁻³] in THF.

6.4.1 REACTIONS OF ANTIMONY TRIS(DIMETHYLAMIDE)

All of the reactions of [Sb(NMe₂)₃] were carried out by the general procedure outlined here.

The guanidine was weighed into a Schlenk, then dried under dynamic vacuum for twenty minutes then an atmosphere of argon was introduced. Addition of toluene dissolved the guanidine though gentle warming was sometimes required to ensure complete dissolution. To this the [Sb(NMe₂)₃] solution was carefully added via syringe.

The details of the individual reactions will relate what occurred after addition and also what efforts were made in order to obtain X-ray quality crystals.
6.4.1.1 One equivalent of tri-substituted guanidine to [Sb(NMe$_2$)$_3$]

Reaction with Tri-p-tolylguanidine

Tri-p-tolylguanidine (0.82 g, 2.5 mmol)  
[Sb(NMe$_2$)$_3$] solution (1.29 cm$^3$, 0.635 g, 2.5 mmol)  
Toluene (10 cm$^3$).

Upon addition the colour changed instantly to yellow and after 1 hour stirring at room temp. to orange. Reduction in solvent volume (ca. 5 cm$^3$) resulted in a turbid solution. Dilution with hexane (20 cm$^3$) caused some precipitation though this redissolved upon warming to give a clear, yellow solution. Storage overnight at room temperature produced non-crystalline material. Rewarming dissolved this and the Schlenk was left in a warm water bath to cool slowly though again precipitation occurred. THF (1 cm$^3$) was added to slow crystallisation but on cooling no solid obtained. Storage at 5°C caused rapid precipitation so after rewarming to dissolve solid, Schlenk was insulated in order to slow cooling and promote crystallisation. After three days at 5°C small oil droplets had formed which crystallised over the space of a week to yield X-ray quality crystals. An X-ray diffraction study was set-up but during data collection the cryostream failed and the crystal decomposed.

This reaction was repeated on a larger scale.

Tri-p-tolylguanidine (1.64 g, 5.0 mmol)  
[Sb(NMe$_2$)$_3$] solution (2.59 cm$^3$, 1.27 g, 5.0 mmol)  
Toluene (10 cm$^3$).

Upon addition of [Sb(NMe$_2$)$_3$] effervescence was observed, while the solution turned through yellow to orange. After stirring for one hour the solution was filtered through Celite to remove decomposition and produced a clear, orange solution. The solvent volume was reduced to 5 cm$^3$ then hexane (25 cm$^3$) was added which precipitated a yellow solid. Warming of the solution redissolved the solid though on cooling a thick oil formed which did not crystallise at 0 or -30°C. The oil was
dissolved by warming and THF (1 cm³) was added but a thick oil formed on cooling. Further THF (1 cm³) was added though no crystals were obtained.

*REACTION WITH TRIS((S)-(--)−α−METHYLBENZYL)GUANIDINE*

Tris((s)-(--)−α−methylbenzyl)guanidine (0.93 g, 2.5 mmol)  
[Sb(NMe₂)₃] solution (1.29 cm³, 0.635 g, 2.5 mmol)  
Toluene (10 cm³).

No colour change observed upon addition of [Sb(NMe₂)₃] and only slight yellowing over period of two days. The reaction mixture was warmed at 50°C for four hours though no colour change was observed so the temperature was increased and the mixture refluxed for one hour. Filtration through Celite to remove decomposition yielded an orange solution, which upon removal of the solvent *in vacuo* gave an orange oil. Hexane (20 cm³) added though not all soluble so dried and ether (10 cm³) added to dissolve. Storage at 5°C yielded no solid so hexane (5 cm³) added and storage at 5°C caused precipitate to form. Warming of the solution dissolved this and upon storage at room temp. only precipitate formed.

*SYNTHESIS OF [Sb((Pr′N)₂CNHPr′)]{(Pr′N)₂CNPr′} 61.*

Triisopropylguanidine (0.928 g, 5.0 mmol)  
[Sb(NMe₂)₃] solution (2.6 cm³, 1.27 g, 5.0 mmol)  
Toluene (10 cm³).

Over a period of two hours the solution was gently warmed and became yellow in colour. The solvent was removed *in vacuo* then residue was dissolved in warm hexane (25 cm³) and filtered through Celite to give a clear yellow solution. The volume was reduced to *ca. 5 cm³* and the resulting microcrystalline precipitate redissolved by warming. Gradual cooling in a water bath over two days provided X-ray quality crystals of 61 (*ca. 10%*). CHN: C₂₂H₄₃N₆Sb requires C 49.1, H 8.80, N 17.1; Found C 48.18, H 8.81, N 16.43; ¹H NMR (250 MHz, d₆-benzene) δ 0.7-1.6 (m, 36H, CH(CH₃)₂), 3.34 (br, 2H, CH(CH₃)₂/NH), 3.72 (spt, 2H, CH(CH₃)₂), 4.12 (spt, 1H, CH(CH₃)₂), 4.35 (spt, 1H, CH(CH₃)₂), 4.83 (spt, 1H, CH(CH₃)₂).
Crystal Data for 61.

Data were collected on a Siemens-Stoe AED diffractometer using an oil coated crystal\(^{6(20)}\) of dimensions 0.2 x 0.2 x 0.2 mm using the \(\theta-\omega\) method (4.04 = \(\theta = 22.73^\circ\)). Of a total of 6438 reflections collected, 4985 (\(R\_int\) 0.026) were independent. The crystal studied was intimately twinned, giving a diffraction pattern approximating to 6\(/mmm\) (\(D_{ob}\)) symmetry. Twin refinement in space group \(P3_2\1\_2\) with [1-10] as the twin axis gave 56.46(9)% as the contribution of the major component and 0.03(3) as the Flack \(x\)-parameter, indicating that both twins have the same correct absolute structure. No conclusions may be drawn about the chirality of the other crystals in the batch. The structure was solved by Patterson methods, and refined by full-matrix least squares on \(F^2\) to final values of \(R_1 = 0.027\) [for 4985 data with \(F > 4\sigma(F)\)] and \(wR_2 = 0.070\) (all data) \([R_1 = \Sigma|F_o - F_e|/\Sigma|F_o|, wR_2 = \{\Sigma w(F_o^2 - F_e^2)^2/\Sigma wF_o^4\}\}^{0.5}, w = 1/\{\sigma^2(F_o^2) + (0.040P)^2 + 4.26P, P = (F_o^2 + 2F_e^2)/3\}.\(^6\21\) Largest difference between peak and hole in the final difference map, 0.42, -0.38 e Å\(^3\). The hydrogen-bonded N-H hydrogens were placed in calculated positions and allowed to ride between their respective nitrogen atoms with a site occupancy of 0.5.

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Table 6.2. Crystallographic Data for 61.
6.4.1.2 TWO EQUIVALENTS OF TRI-SUBSTITUTED GUANIDINE TO [Sb(NMe₂)₃]

**REACTION WITH TRI-P-TOLYL GUANIDINE**

Tri-p-tolylguanidine (0.66 g, 2.0 mmol)
[Sb(NMe₂)₃] solution (0.52 cm³, 0.25 g, 1.0 mmol)
Toluene (10 cm³).

Immediate colour change from colourless to yellow to orange. After stirring for thirty minutes filtration through Celite gave a clear orange solution. While reducing solvent volume (ca. 5 cm³) a large quantity of bright yellow solid precipitated from solution. Redissolved upon warming though on cooling to room temp. a fluffy precipitate formed. Toluene (5 cm³) was added to slow solidification and the solution was slowly cooled in a water bath over three days however no precipitate formed at all. Storage at 5°C also produced no solid though storage at -30°C caused precipitation. The volume of toluene was slightly reduced though precipitation occurred at 5°C. Addition of THF (1 cm³) to slow solidification further failed to prevent precipitation. Unfortunately, due to lack of time no further attempts at crystallisation could be undertaken.

**REACTION WITH TRICYCLOHEXYL GUANIDINE**

Tricyclohexylguanidine (1.53 g, 5.0 mmol)
[Sb(NMe₂)₃] solution (1.29 cm³, 0.635 g, 2.5 mmol)
Toluene (10 cm³).

Following addition slight colourisation of the solution was observed while stirring at room temp. over a period of two hours. The reaction mixture was filtered to remove decomposition and a clear, almost colourless solution was obtained. Reduction of solvent volume and cooling to -30°C yielded no precipitate so solvent was removed in vacuo to dryness. The tacky white residue was dissolved in hexane (20 cm³) and storage at 5°C precipitated a white solid which was shown by IR spectroscopy to be free ligand (υC=N 1640 cm⁻¹). After filtration and cooling more white precipitate was obtained and this was also identified to be free ligand (υC=N 1640 cm⁻¹). The
combined weight of the isolated guanidine (1.12 g) indicated that no reaction had taken place at room temperature.

When repeated the reaction was performed on a smaller scale.
Tricyclohexylguanidine (0.76 g, 2.5 mmol)
[Sb(NMe₂)₃] solution (0.65 cm³, 0.32 g, 1.25 mmol)
Toluene (10 cm³).

Following addition of [Sb(NMe₂)₃] the reaction mixture was heated to reflux for twenty-four hours. During this time no appreciable colour change was observed though some decomposition occurred. After filtration a dull, yellow solution was obtained from which no crystals could be grown. Solvent was removed to dryness, the residue taken up in hexane (10 cm³) and filtered to remove grey solid. No crystals were obtained at room temp. and storage at 5°C produced a white precipitate, presumed to be free ligand.

6.4.1.3 Reaction of Tetra-substituted Guanidine with [Sb(NMe₂)₃]

Reaction of one equivalent diethyl-diphenylguanidine with [Sb(NMe₂)₃].
Diethyl-diphenylguanidine (0.67 g, 2.5 mmol)
[Sb(NMe₂)₃] solution (1.29 cm³, 0.635 g, 2.5 mmol)
Toluene (10 cm³).

Upon addition no colour change was observed and after stirring for two hours only a pale yellow colour was visible in the reaction mixture. Addition of hexane (10 cm³) caused no precipitation so solvent was removed to dryness and the residue taken up in pure hexane (30 cm³) giving a clear solution. Storage overnight at 5°C yielded a white solid identified as free ligand from its IR spectrum (vC=N 1610 cm⁻¹).

The reaction was repeated on the same scale, though after addition the mixture was refluxed for twenty-four hours. During this time the solution turned cloudy and a grey precipitate settled out. Filtration gave a clear, yellow solution, from
which the solvent was completely removed, yielding a sticky oil which completely dissolved in hexane (10 cm$^3$). The solvent volume was reduced until the product crashed out of solution. Rewarming completely dissolved the solid though upon standing at room temp. only a fine precipitate was obtained. The solution was filtered and the clear, bright yellow solution obtained yielded very small crystals upon standing. Attempts to increase the size by cooling slowly and diluting the solution failed and no crystals of sufficient size for an X-ray study were obtained.

Reaction of two equivalents diethyl-diphenylguanidine with [Sb(NMe$_2$)$_3$].

Diethyl-diphenylguanidine (1.34 g, 5.0 mmol)  
[Sb(NMe$_2$)$_3$] solution (1.29 cm$^3$, 0.635 g, 2.5 mmol)  
Toluene (10 cm$^3$).

After addition of [Sb(NMe$_2$)$_3$] the reaction mixture was stirred at room temp. for three hours and during this period no colour change was observed. The solvent was removed in vacuo to leave a white solid which was insoluble in hexane. This was isolated and IR analysis confirmed that it was the free ligand (υC=N 1610 cm$^{-1}$).

6.4.2 Reactions of Tin bis(dimethylamide)

Reaction with Triisopropylguanidine

To [Sn(NMe$_2$)$_2$] (0.52 g, 2.5 mmol), toluene (10 cm$^3$) was added though not all soluble so THF (1 cm$^3$) added to aid dissolution. To this mixture a solution of triisopropylguanidine (0.46 g, 2.5 mmol) in toluene (5 cm$^3$) was added via cannula. No obvious colour change followed addition and the solution remained the same after stirring for twenty-four hours at room temp. Warming of the mixture to 80°C for five hours caused precipitation of a grey solid which was removed by filtration yielding a pale yellow solution. Evaporation of solvent in vacuo produced a dark, yellow oil which was not crystallised.
REACTION WITH TRI-p-TOLYLGUANIDINE

[Sn(NMe₂)₂] (0.52 g, 2.5 mmol) was partially dissolved in a mixture of toluene (10 cm³) and THF (1 cm³). Addition of a solution of tri-p-tolylguanidine (0.82 g, 2.5 mmol) in toluene (5 cm³) created no visible change in the reaction mixture. The mixture was heated to reflux for five hours though no colour change was observed over this period. Removal of solvent yielded a yellow powder which was soluble in THF but not hexane. Crystallisation was attempted by dissolving in the minimum volume of THF (ca. 4 cm³) and carefully layering with hexane (30 cm³) however no crystals were obtained. Once the solvents has mixed the solution was stored at 5°C for six days though no crystals were obtained.

6.4.3 REACTIONS OF DICYCLOPENTADIENYL Tin

REACTION WITH TRI-p-TOLYLGUANIDINE

Tri-p-tolylguanidine (0.99 g, 3.0 mmol) was dissolved in THF (10 cm³) then cooled to -78°C. To this "BuLi (4.0 cm³ of a 15% solution in hexane, 6.0 mmol) was added with a slight yellowing of the solution and which, upon warming to room temperature, formed a white solid. Cp₂Sn (0.89 cm³ of a 2.25 mol dm⁻³ solution, 2.0 mmol) was added dropwise at room temp. initially producing a yellow solution. During addition the white precipitate was steadily consumed and after addition an orange solution was obtained. Warming of the reaction mixture (ca. 50°C) caused a precipitate to form which surprisingly redissolved upon returning to room temp. The THF volume was reduced (5 cm³) and to the clear solution ether (3 cm³) was added dropwise until precipitate formed at room temp. Cooling of this solution (-78°C) caused the precipitate to dissolve and the solution was left to slowly return to room temp. however no crystals were obtained.

REACTION WITH TRICYCLOHEXYL GUANIDINE

Following an analogous procedure, Cp₂Sn (0.89 cm³ of a 2.25 mol dm⁻³ solution, 2.0 mmol) was added to a solution of tricyclohexylguanidine (0.916 g, 3.0 mmol) in THF (10 cm³) previously lithiated with "BuLi (4.0 cm³ of a 15% solution in
hexane, 6.0 mmol). Upon addition a yellow solution formed immediately which gradually deepened to orange while a white precipitate formed also. This did not redissolve upon warming or cooling so the reaction mixture was filtered, producing a clear orange solution. Initial attempts at crystallisation from THF solutions failed and time prevented any further attempts.

**REACTION WITH TRIS((S)-(−)-α−METHYLBENZYL)GUANIDINE**

Again following the same procedure, tris((s)-(−)-α–methylbenzyl)guanidine (1.11 g, 3 mmol) in THF (10 cm$^3$) was deprotonated by $^t$BuLi (4.0 cm$^3$ of a 15% solution in hexane, 6.0 mmol). Addition of Cp$_2$Sn (0.89 cm$^3$ of a 2.25 mol dm$^{-3}$ solution, 2.0 mmol) formed a pale yellow solution which turned pale orange after stirring for one hour at room temp. Some white precipitate formed which was removed by filtration though celite. To the resulting clear solution ether (3 cm$^3$) was added dropwise until the mixture turned cloudy. Warming of this caused all precipitate to dissolve though gradual cooling to room temp. and 0° failed to provide crystals.
6.5 REFERENCES


List of Courses Attended

Lecture Courses / Workshops

- Introduction to Daresbury Databases, 1996: 4 lectures
- EPR Spectroscopy, 1996: 1 lecture
- Synthesis of Fine Chemicals, 1996: 4 lectures
- Introduction to Patents, 1997: 4 lectures
- Ligand Synthesis, 1998: 5 lectures
- Introduction to Beilstein Database, 1998: 2 lectures

Conferences / Meetings

- RSC Dalton Meeting (Edinburgh 1996): 1 day
- RSC Scottish Dalton Meeting (Edinburgh, 1997): 1 day
- XIIth FECHEM Conference on Organometallic Chemistry (Prague, 1997): 5 days
- Universities of Scotland Inorganic Club (Edinburgh, 1997): 2 days
- RSC Warwick Catalysis Meeting (Warwick, 1998): 1 day

In addition I have attended departmental colloquia and inorganic section meetings throughout the period of my study (1995 - 1998).
During the second year of my PhD I studied at the University Of Kaiserslautern, Germany for three months (June -September 1997). I worked under the supervision of Prof. Dr. Cornelius G. Kreiter investigating the photochemical reactions of alkynes with manganese tricarbonyl complexes.

The first project I was given to study was the reaction of \([\eta^5\text{-cyclooctatrienyl}]\text{tricarbonylmanganese(0)}\) a with alkynes, following on from the analogous reactions that had been studied with \([\eta^5\text{-cyclooctadienyl}]\text{tricarbonylmanganese(0)}\). However before these reactions could be studied it was required to synthesise the manganese complex. This was attempted by two routes (see Fig. I): photochemical reaction of cyclooctatriene with dimanganese decacarbonyl and the thermal reaction of cyclooctatetraene with pentacarbonylmanganese hydride. Unfortunately both of these routes proved unsuccessful which was in contrast to the high yielding route to the cyclooctadienyl derivative. These problems may have arisen as a result of the higher steric constraints imposed by the additional double bond within the cyclooctatrienyl fragment.

![Figure I.](image)

The second project I worked on in Kaiserslautern was the reaction of alkynes with \([\eta^5\text{-napthalyl}]\text{tricarbonylmanganese(0)}\) b. The synthesis of this starting material had already been optimised although the maximum yield of b available was only 150 mg per reaction which severely limited the time available to study its reactions. Solutions of b in toluene and acetonitrile were photolysed in the
presence of various di-substituted alkynes (R = Me, Ph, CO₂Me) (see Fig. II). The reactions were followed by IR spectroscopy and the parent bands were observed to recede with new carbonyl stretches forming. Separation of the products by column chromatography was attempted though analysis of the resultant solids revealed that no pure products were obtained. The substitution of a carbonyl in b by a phosphine was also studied though again no clean product was isolated from the reactions.
Publications

Publications to which I have contributed and are directly related to the work described in this thesis.

“Synthesis and structure of [Sb{(Pr'N)₂CNHPr'}{(Pr'N)₂CNPr'}]; a distorted trigonal-bipyramidal antimony(III) complex with a helical hydrogen-bond network”
Philip J. Bailey, Robert O. Gould, Christopher N. Harmer, Stuart Pace, Alexander Steiner and Dominic S. Wright.

“Guanidines as neutral monodentate ligands; syntheses and crystal structures of [CoCl₂{(PhN=CH-NHPh)₂}₂] and [Ag{(PhN=CH-NHPh)₂}[O₃SCF₃]”
Philip J. Bailey, Keith J. Grant, Stuart Pace, Simon Parsons and Lisa J. Stewart.
1,2,3-Trisopropylguanidine [(PrN)2CNHPr] reacts with antimony tris(dimethylamide) [Sb(NMe2)3] to provide [Sb{(Pr'N)2CNHPr}[(PrN)2CNPr]] 1, a distorted trigonal-bipyramidal complex in which the Sb is chelated by a (CNPr')2—dianion and a [(Pr'N)2CNHPr]—monoanion; in the solid state the complexes form helices by N–H⋯N hydrogen bonding of the single proton.

Our recent interest in trisubstituted guanidines and their anions as ligands has led to the characterisation of a number of new complexes which have demonstrated the flexibility of this new ligand system in both chelating and bridging coordination modes. The ligands also exhibit a marked ability to stabilise higher oxidation states in transition-metal complexes. The ability of the system to coordinate as a neutral (H3L), monoaionic (HL—) or dianionic (L2—) ligand, and the presence of ionisable protons on the former two, adds to its flexibility. Hydrogen bonding plays an important role in much of the chemistry of guanidines and molecules containing the guanidine unit such as the nucleic acid base guanine, and we have thus become interested in the hydrogen-bonding properties of metal coordinated guanidines containing residual protons. Here we report a complex containing a single hydrogen which is formed by chelation of a trivalent metal by two trisubstituted guanidines, one a monoanion and the other a dianion, thus providing an N–H hydrogen-bond donor on one ligand and a lone nitrogen hydrogen-bond acceptor on the other.

Treatment of 1,2,3-trisopropylguanidine with 1 mol. equiv. of [Sb(NMe2)3]5 in toluene solution provides a yellow solution. Reduction of this solution to dryness in vacuum and dissolution of the residue in warm hexane followed by filtration, concentration and cooling provided highly air-sensitive crystals of [Sb{(Pr'N)2CNHPr}[(PrN)2CNPr]] 1 in 10% yield.† The presence of both the anion HL— and dianion L2— is confirmed by the 1H NMR spectrum of 1 which shows that there are five independent isopropyl groups in the ratio 1:1:1:1:2, consistent with free rotation only about the uncoordinated C–NHPr bond of the HL— ligand whilst the C=NPri bond of the L2—remains static. The formation of 1, which retains an N–H hydrogen despite the presence of sufficient metalling agent in the reaction mixture to remove all such hydrogens, is worthy of note and may be a result of preferential crystallisation of the hydrogen-bonded partially metallated species, vide infra, and explain its low yield. Unfortunately, the extreme air sensitivity of 1 prevented the recording of any IR spectra.

Crystals of 1 are chiral with space group P32 1 or P32 121 and a low-temperature X-ray crystallographic study shows that there are two independent, but chemically equivalent, molecules in the unit cell which differ only marginally in the conformationations of their isopropyl groups and in their bond lengths and angles. One molecule lies on a twofold rotational axis relating the two ligands (Fig. 1), whilst the other (molecule 2, not shown) lacks this axis. The complex consists of [Sb{(PrN)2CNHPr}[(PrN)2CNPr]] molecules in which each SbIII centre is formally chelated by a monoanion HL— and a dianion L2— ligand. The molecular structure of 1 is consistent with the ten-electron count of the Sb centre and can best be described as a heavily distorted trigonal-bipyramidal Sb molecule with the fifth coordination site being occupied by the lone pair. In both independent molecules the SbIII centres are asymmetrically coordinated by the two guanidine ligands [e.g. Sb(1)–N(11) 2.227(6) Å, Sb(1)–N(13) 2.069(6) Å]. This pattern of bond lengths is consistent with the description of the structure as distorted trigonal bipyramidal since in this geometry each ligand would be coordinated to an axial and an equatorial position. The nature of the distortion can be appreciated if it is considered that in this structure trigonal-bipyramidal geometry requires the chelating angle at the metal (N–Sb–N) to be 90°, whilst in 1 far more acute angles at Sb are found as a consequence of the geometric constraints arising from the chelation by the rigid guanidine ligands [e.g. N(11)–Sb(1)–N(13) 62.0(2)°]. The result of this is that the N–Sb–N angle between the axial N centres is distorted from the 180° to

![Fig. 1 Molecular structure of 1. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): molecule 1: Sb(1)–N(11) 2.227(6), Sb(1)–N(13) 2.069(6), C(10)–N(11) 1.372(10), C(10)–N(12) 1.311(11), C(10)–N(13) 1.342(10), N(11)–Sb(1)–N(13) 62.0(2), N(11)–Sb(1)–N(11a) 140.3(3), N(13)–Sb(1)–N(13a) 140.5(3), N(13)–Sb(1)–N(11a) 93.3(2), N(12)–N(12a) 3.148(12), N(12)–H(12)–N(12a) 160; molecule 2: N(31)–Sb(2) 2.320(6), N(33)–Sb(2) 2.098(6), N(41)–Sb(2) 2.133(6), N(43)–Sb(2) 2.050(5), C(30)–N(33) 1.325(9), C(40)–N(43) 1.402(9), C(40)–N(42) 1.273(9), C(40)–N(43) 1.381(9), N(31)–Sb(2)–N(33) 59.9(2), N(41)–Sb(2)–N(43) 63.9(2), N(41)–Sb(2)–N(31) 140.2(2), N(33)–Sb(2)–N(43) 104.2(2), N(33)–Sb(2)–N(41) 92.7(2), N(31)–Sb(2)–N(43) 93.4(2), N(32)–N(42) 3.125(12), N(32)–H(32)–N(42) 142, N(42)–H(42)–N(32) 144.](image)
Fig. 2 Stereoview showing the association of molecules of 1 via N—H···N hydrogen bonds into helices. Symmetry transformations used to generate equivalent atoms a, x,y,z; a, x,y,z−1/3.

140.3(3)° for N(11)···Sb(I)···N(11a)) and that for the equatorial N centres is distorted from the 120° [to 104.5(3)° for N(13)···Sb(I)···N(13a)] required for ideal trigonal-bipyramidal geometry. The distorted trigonal-bipyramidal geometries of the Sb(III) centres of 1 are very similar to those observed for the central metal atom in the [(Me2NN2Sb(NC6H4H2)2)2Sb]− monocation,6 which is the only other structurally characterised unit containing an Sb(III) centre four-coordinated by nitrogen ligands.

Although the ligands in each molecule of 1 must formally be a monoanion and a dianion to provide the necessary trianionic ligand set for the Sb(III) centre, in the crystal they cannot be distinguished in this way since each of the uncoordinated NP1-groups is involved in hydrogen bonding to an adjacent molecule with an N···N distance of 3.184(12) Å and N—H···N angle of 160°. As a consequence of the alignment of these groups, which is dictated directly by the distorted trigonal-bipyramidal geometry present in the molecular units of 1, the resulting hydrogen-bonded H···L-Sb-L···H···L-Sb-L···H··· chains form left-handed helices through the crystal studied with three molecules of 1 per 360° turn (Fig. 2). It is probable that other crystals have the opposite chirality and hence right-handed chirality. Helical association of monomer units has been identified in a few polymeric phosphido and amido lithium complexes7 and packing of molecules of [Ru3(CO)9{1,2-t-NCH2CH(NMe2)2}]8 exclusively into β helices occurs in the solid state.8 However, helical packing or association of molecules is extremely rare in transition and main group metal compounds and, to our knowledge, the helical hydrogen-bonded association found in 1 is unprecedented for any metallo-organic compound.

We gratefully acknowledge the EPSRC (studentships for C. N. H. and S. P.), The Leverhulme Trust (P. J. B.), The Royal Society (P. J. B., D. S. W.) and The European Community (Fellowship for A. S.) for financial support.

Footnotes
* E-mail: philip.bailey@ed.ac.uk
† 1,2,3-Trisopropylguanidine (0.928 g, 5.0 mmol) was dissolved in toluene (10 cm3) and 2.6 cm3 of a 1.93 M solution of [Sb(NMe2)3] in toluene (1.275 g, 5.02 mmol) was added by syringe under argon. Over a period of 2 h the solution became yellow and the solvent was then removed in vacuo. The residue was dissolved in warm hexane (25 cm3) and filtered through Celite to give a clear yellow solution. The volume was reduced to ca. 5 cm3 and the resulting microcrystalline precipitate redissolved by warming. Gradual cooling in a water bath over two days provided X-ray quality crystals of 1 (ca. 10%). (Found: C, 48.2; H, 8.81; N, 16.4. C20H43N6Sb requires C, 49.1; H, 8.80; N, 17.1%).1H NMR (250 MHz) in [1H2]-benzene: δ 6.0–1.6 ppm, 36 H, C(H2)(1); 3.34 [2 H, CH(CH3)2(NH)2], 3.72 [2 pt, 2 H, CH(CH3)2], 4.12 [pt, 1 H, CH(CH3)2], 4.35 [pt, 1 H, CH(CH3)2], 4.83 [pt, 1 H, CH(CH3)2].
‡ Crystal data for 1: C20H43N6Sb, Mw = 489.35, trigonal, space group P32, a = 17.356(2), b = 17.356(2), c = 21.919(4) Å, α = 90°, β = 120°, γ = 120°, Z = 3. A total of 6438 reflections collected, 4985 (Rint = 0.026) were independent. The crystal studied was intimately twinned, giving a diffraction pattern approximating to 1/mmm (Da) symmetry. Twin refinement in space group P32 with [110] as the twin axis gave 56.46(9)% as the contribution of the major component and 0.03(3) as the Flack x-parameter, indicating that both twins have the same correct absolute structure. No conclusions may be drawn about the chirality of the other crystals in the batch. The structure was solved by Patterson methods, and refined by full-matrix least squares on F2 to final values of R1 = 0.027 (for 4985 data with F > 4σ(F)) and wR2 = 0.070 (all data) [R1 = 0.041, wR2 = 0.077; P = (Σw(F2)− F2)/Σw(F2)1/2 = 1.016; F2 = 0.446]. P. J. Bailey, L. A. Mitchell and S. Parsons, J. Chem. Soc., Dalton Trans., 1996, 2839.

References

Received in Basel, Switzerland, 10th March 1997; Com. 70/1675A 1162 Chem. Commun., 1997
Two complexes exhibiting monodentate metal co-ordination of a neutral guanidine have been synthesized and structurally characterized. Treatment of CoCl₂ with 1,2,3-triphenylguanidine in tetrahydrofuran solution produced the tetrahedral complex [Co{(PhN)C(NHPh)₂}]₂Cl₂ 1 in which the guanidine ligands are co-ordinated through their imine nitrogen atoms alone. Similarly, treatment of the guanidine with Ag[SO₃CF₃] in toluene provided the linear complex [Ag{(PhN)C(NHPh)₂}]₂[SO₃CF₃]₂ in which the triflate counter ion remains uncoordinated, but is hydrogen bonded to the guanidine hydrogen atoms. Both complexes have been characterized by X-ray crystallography.

The nitrogen analogues of carboxylic acids, amidines (RN=CR—NHR) and triazenes (RN=N—NHR), have been shown to be excellent ligands for transition metals, in particular as anionic chelating or bridging amidinates and triazenates. However, their behaviour as neutral monodentate ligands is comparatively uncommon, although a number of such complexes have been characterized. The increased basicity (donor strength) of the nitrogen donors over oxygen, and the added flexibility provided by manipulation of the electronic and steric properties of the R groups, are features of these ligands which have been exploited on many occasions. In particular, the potential of complexes in which the sterically demanding bis-(trimethylsilyl)benzamidinate ligand [PhC(NSiMe₃)₂]⁻ displaces a cyclopentadienyl ligand to provide new unsaturated complexes has attracted considerable attention over recent years. Guanidines [RN=C(NHRR)₂] bear the same relationship to carboxylic acid as amidines and triazenes do to carboxylic acids, and as such should be excellent ligands given the above considerations. Furthermore, there exists the possibility of a second deprotonation to provide a dianionic ligand [C(NR)₃]⁻, the nitrogen analogue of carbonate, which is unavailable to the carboxylic acid analogues. Carbone is a highly versatile ligand which has been structurally characterised in a multitude of mono-, di- and tri-hapto co-ordination modes, and it is therefore surprising that the potential of guanidines as ligands with a diverse co-ordination chemistry is only now beginning to be appreciated.

Our initial interest in the potential of guanidines and their analogs as ligands was prompted by the prospect that the [C(NR)₃]⁻ dianion might exhibit an η²-co-ordination mode in which all three nitrogen donors are bound to a single metal ion. This is a co-ordination mode unknown for the carbonate ligand, but its ubiquity for the trimethylmethane ligand [C(CH₃)₃]³⁻, the carbon analogue of this system, fuelled our expectation that it might also be observed for the nitrogen ligand. Although we have yet to demonstrate the existence of such a co-ordination mode for the guanidine dianion, we have now developed the co-ordination chemistry of guanidines to a considerable extent. We have previously reported ruthenium and rhodium complexes containing chelating guanidinate ligands, and the redox pair [M₂(η²-(NPh)₃NMePh)₃]³⁺, which gave the first indications of the flexible donor properties of these ligands. In addition we have characterised a number of main-group complexes containing both guanidine mono- and di-anions. Here we report the syntheses and structural characterisation of rare examples of complexes containing a guanidine co-ordinated as a neutral monodentate ligand. To our knowledge there are only two previous examples of complexes containing monodentate guanidine ligands which have been structurally characterised, and in both of these the ligand reported here is, in contrast, a 1,2,3-trisubstituted guanidine [(R₂N)₂C=NH].

Results and Discussion

Our previous observations of the reactivity of 1,2,3,triphenylguanidine with the metal halide complexes [{Rh(n-2-C₅Me₃)Cl₂} and {Ru(n-2-MeC₆H₄Ph₂-p)Cl₂}] had shown that, in addition to cleaving the chloro-bridges, the guanidine also acts as a base to provide a chelating guanidinate ligand with concomitant formation of the guanidinium chloride. Indeed, treatment of these dimers with 4 molar equivalents of the guanidine in toluene solution rapidly leads to precipitation of the salt and formation of the guanidinate complexes in good yield at room temperature. Given the observation that amidines and triazenes can act as neutral imine donors to provide tetrahedral complexes with transition-metal dihalides, we were interested to investigate the possibility that guanidines could behave in a similar fashion.

[Co{(PhN)C(NHPh)₂}₂Cl₂] 1

Treatment of CoCl₂ with 2 molar equivalents of 1,2,3-triphenylguanidine in tetrahydrofuran (thf) under reflux provides a bright blue solution of [Co{(PhN)C(NHPh)₂}₂Cl₂] 1.

which may be obtained as the crystalline bis(dichloromethane) solvate in 77% yield by slow evaporation of a dichloromethane-hexane solution. The infrared spectrum of this complex as a Nujol mull shows the v(C=N) mode of the co-ordinated guanidine at 1626 cm\(^{-1}\) which compares with a value of 1637 cm\(^{-1}\) for the free guanidine. Previous studies of transition-metal guanidine complexes have shown a similar reduction in C=N stretching frequency.\(^{14,15}\) Thus, a low-energy shift of between 60 and 67 cm\(^{-1}\) has been observed for the 1,1,3,3-tetramethylguanidine (L) complexes \([ML_4]^2[ClO_4]_2\) \((M = Co, Cu or Zn)\) and \([CoCl_2(NC_5H_4OMe-2)_2]\) which is not shown, has similar metrical parameters

![Fig. 1 Thermal ellipsoid plot of \([Co((PhN)C(NHPh)\_2)\_2Cl]\) 1 showing the atom numbering scheme. A second molecule in the unit cell, which is not shown, has similar metrical parameters](image)

The Co-Cl bond lengths are only slightly longer than in the analogous compound with \([CoCl_2(NC_5H_4OMe-2)_2]\) 2.284(2) Å, 2.284(2) Å, 1.312(8) Å, 1.312(8) Å, and \([CoCl_2(NC_5H_4Me-4)_2]\) 2.284(2) Å, 2.284(2) Å, 1.312(8) Å, 1.312(8) Å, 1.375(8) Å, 1.375(8) Å, and \([CoCl_2(NC_5H_4Ph-2)_2]\) 2.284(2) Å, 2.284(2) Å, 1.312(8) Å, 1.312(8) Å, respectively. However, the chemical significance of these observations is questionable since the bond angles around the cobalt are however observed for the guanidine and formamidine complexes; whilst the N-Co-N angles for the two complexes are almost identical \([113.2(2)\) and 113.3(2)\(^{\circ}\) respectively], the Cl-Co-Cl angles differ markedly \([105.3(2)\) and 115.1(6)\(^{\circ}\) respectively]. However, the crystal structure determination shows that complex 1 contains two independent molecules per unit cell, solvated by two molecules of CH\(_2\)Cl\(_2\). In all cases, the differences in bond lengths for the two molecules are not crystallographically significant.

![Fig. 2 Thermal ellipsoid plot of \([Ag{(PhN)C(NHPh)\_2}][SO_4Cl_2]_2\) 2 showing the atom numbering scheme. The silver ion is located at an inversion centre which relates the two ligands. A second molecule in the unit cell, which is not shown, has similar metrical parameters](image)

The reaction of silver triflate with I,2,3-triphenylguanidine proceeds at reflux in toluene to provide the toluene-soluble complex \([Ag{(PhN)C(NHPh)\_2}][SO_4Cl_2]_2\) which may be characterised as well formed colourless blocks by layering with hexane. The infrared spectrum of 2 shows the C=N stretching band at 1618 cm\(^{-1}\) and the v(N-H) modes as two sharp absorptions at 3366 and 3304 cm\(^{-1}\). A crystal structure determination shows the crystals of 2 to contain two independent molecules per unit cell each consisting of a linear \([AgL_2]^+\) complex with an associated triflate counter ion. Complex 2 is illustrated in Fig. 2 and selected bond lengths and angles are given in Table 2. Both
Table 2  Selected bond lengths (Å) and angles (°) for [Ag(PhN)-
C(NHPh)2]2SO4CF3]

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(1)-N(11)</td>
<td>2.135(8)</td>
</tr>
<tr>
<td>N(11)-C(11)</td>
<td>1.36(1)</td>
</tr>
<tr>
<td>C(11)-N(21)</td>
<td>1.32(1)</td>
</tr>
<tr>
<td>N(21)-C(12)</td>
<td>1.35(1)</td>
</tr>
<tr>
<td>C(12)-N(31)</td>
<td>1.36(1)</td>
</tr>
<tr>
<td>N(31)-C(13)</td>
<td>1.32(1)</td>
</tr>
<tr>
<td>Ag(2)-N(12)</td>
<td>2.146(8)</td>
</tr>
<tr>
<td>N(12)-C(12)</td>
<td>1.35(1)</td>
</tr>
<tr>
<td>C(12)-N(22)</td>
<td>1.36(1)</td>
</tr>
<tr>
<td>N(22)-C(13)</td>
<td>1.36(1)</td>
</tr>
</tbody>
</table>

complexes possess an inversion centre at silver which relates the
ligands, and although the differences in some of the metrical
data for these two complexes is crystallographically signifi-
cant the essential features are the same for the two, and con-
sequently only the complex containing Ag(1) is discussed in
detail. The Ag-N distances in the two independent molecules
[2.135(8) and 2.146(8) Å]2 are intermediate between those
found for the bis(ammine) complex [Ag(NH3)2][ClO4]2 [2.112(6)
and 2.117(6) Å]23 and the polymeric ethane-1,2-diamine com-
plex [{Ag(en)}2][ClO4]2 [2.17(1) Å]24 both of which also
exhibit essentially linear co-ordination of the silver ion. As far
as the ligand is concerned, the most closely related, structurally
characterised complex is the recently reported three-co-
ordinate silver formamidine complex [Ag(PhN=CH-NHPh)2-
(O2SCF3)]2 in which the Ag-N distances were found to be
2.179(4) and 2.206(4) Å, significantly longer than those in 2.
Although in this complex, as in 2, the silver is co-ordinated by
two Ph-N=C imine nitrogen atoms, the difference in Ag-N dis-
tances between the two may be attributed to the change in the
geometry brought about by the weak co-ordination of triflate in
the formamidine complex (N-Ag-N 142°) rather than by any
difference between the nitrogen ligands. This is supported by our
observation that the Co-N distances in the two tetrahedral
complexes I and [CoCl2((R=NR)NHR)]2 (R = p-tolyl) do not
differ significantly (see above). The anticipated similarity of the
C=O properties of the imine nitrogen atoms of the form-
amidine (PhN=CH-NHPh) and guanidine (PhN=C(NHPh)2)
ligands would suggest that the reason for the difference in co-
ordination environments for the silver ions in the two com-
pounds is steric rather than electronic in origin. Indeed, it is clear
from the structure of 2 that the silver is shielded from further
co-ordination by two flanking phenyl groups on unco-ordin-
ated nitrogens.
Although the NH hydrogens in complex 2 were not directly
located in the crystallographic study, co-ordination of the imine
rather than an amine nitrogen to the silver is indicated by com-
parison of the central C-N bond distances within the ligands.
For molecule 1 these distances are 1.32(1) Å for the carbon to
co-ordinated nitrogen and 1.39(1) Å for the two bonds to the
unco-ordinated nitrogens. The corresponding distances for mole-
cule 2 are 1.29(1), 1.35(1) and 1.36(1) Å respectively. The
[SO4CF3]2- counter ion in 2 is hydrogen bonded via two S=O
oxygenes to the NH hydrogens of the guanidine ligands. The
N-O distances in these N-H...O systems range from
2.912(12) to 3.109(13) Å and the N-H-O angle from 128.5 to
145.3°.

Experimental
General
All reactions were carried out under an atmosphere of dry,
oxygen-free nitrogen using standard Schlenk techniques and
solvents which were dried and distilled under nitrogen immedi-
ately prior to use. The 1,2,3-triphenylguanidine was prepared by
condensation of aniline with diphenylcarbodiimide in toluene solution. The CoCl2 (Aldrich) was dried by heating to
reflux with an excess of thionyl chloride for 30 min followed by
drying at 50 °C under dynamic vacuum for 1 h. The NMR
spectra were recorded on a Bruker AC 250 spectrometer and the
infrared spectra on a Perkin-Elmer Paragon 1000 spectrometer
from samples as Nujol mulls and mass spectra on a Kratos
MS50 TC instrument in positive-ion FAB mode using 3-nitro-
benzyl alcohol as matrix and CsI as calibrator. Elemental ana-
lyses were conducted by the microanalytical service of this
department.

Syntheses

[C(NPhC[N(Ph)H]2)]2. Silver triflate (427 mg, 1.66 mmol) and 1,2,3-triphenylguanidine (955 mg, 3.32 mmol) were placed in a Schlenk tube under nitrogen and aluminium foil was wrapped around the tube to exclude light. Toluene (40 cm3) was added and the mixture heated to reflux for 1 h. The resulting mixture was filtered through a Celite pad to remove a small amount of pale brown material and the resulting very
pale pink solution was reduced to ca. 10 cm3 under vacuum.
The solution was layered with hexane (20 cm3) and allowed to
stand overnight to yield a crop of colourless crystals suitable for
X-ray crystallography (720 mg, 52%) (Found: C, 57.67; H, 4.51;
N, 9.61%). This is consistent with

M = Cl),
\( Z = 8, D_1 = 1.368 \ \text{g} \cdot \text{cm}^{-3}, F(000) = 3592, \text{blue columnar block,} \)
0.58 × 0.29 × 0.29 mm, T = 220 K, m(\text{Mo-K\text{a}}) = 0.818 \ \text{mm}^{-1}. \)

For 2: C_{36}H_{76}AgF,N,O,S, M = 831.66, triclinic, space group
P1, a = 9.802(5), b = 13.760(7), c = 15.864(7) Å, \( \alpha = 86.81(2), \gamma = 75.39(9) ), \)
0.35 × 0.23 × 0.19 mm, T = 220 K, m(\text{Mo-K\text{a}}) = 0.65 \ \text{mm}^{-1}.
Data collection, solution and refinement. Data were collected using Mo-Kα radiation in the range 5 ≤ 2θ ≤ 50° for complex 1 and 5 ≤ 2θ ≤ 45° for 2 on a Stoe Stadi4 diffractometer equipped with an Oxford Cryosystems low-temperature device using ω-θ scans. An absorption correction based on ψ scans was applied for 1 (maximum and minimum coefficients 0.540 and 0.498), R_{int} = 0.1958 (based principally on a weak high-angle data). Owing to rather low crystal quality, characterised by poor peak shapes and high backgrounds, a consistent set of ψ scans could not be obtained for 2, leaving little option but to apply a correction during refinement (DIFABS, correction applied to F^2 maximum and minimum corrections 1.347 and 0.683, respectively). Both structures were solved by direct methods (SIR 92). Complex 1 was refined against F^2 using DIFABS, correction applied to data. The final difference-synthesis maximum and minimum were 0.0639, 0.0759 [based on F^2 and all 14784 data] for 956 parameters. The refinement converged to Ri = 0.2013 (based on F^2 and all 14784 data) for 956 parameters. The final difference-synthesis maximum and minimum were +0.51 and −0.50 e Å^−3, respectively.

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References


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